

COLLECTION OF REPRESENTATIVE COAL REFUSE SAMPLES FOR LEACHATE GENERATION STUDIES

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ABSTRACT

A statistically valid sampling plan with a known degree of precision is necessary to assess the environmental impact of coal cleaning refuse (gob) piles via leaching studies. At two gob piles located in southwestern Illinois a portable drilling rig was used to collect 200 split-spoon samples at various depths and locations. The samples were subjected to the ASTM method A water shake extraction procedure and the concentrations of 30 constituents in the shake test extracts were determined. The extract data were used to determine: 1) the variability of constituent concentrations in the extracts; 2) the effect of sample depth and location on constituent concentrations, 3) the number of samples required to have the sample mean within either 5%, 10%, or 25% of the estimated population mean at a 95% confidence level, and 4) the number of samples required to minimize sample collection and analysis costs and variances.

The pH values of shake test extracts ranged from 1.55 to 5.04. The predominant constituents in the extracts were Al, Ca, Fe, SO_4 , and Zn. Calcium, Co, Mn, Ni, and Zn exhibited the greatest relative solubility on the basis of their weight percentage in these wastes. Univariate statistical analysis indicated differences in constituent concentrations in the extracts related to sample depth. Patterns between constituent concentrations and sample depth allowed some of the data to be grouped into depth zones. Statistically significant differences due to sampling location within a gob pile as well as differences between gob piles were exhibited for most extract constituent concentrations.

The means and variances generated by the extract data and a t distribution were used to calculate the number of samples required for the sample mean to be within a specified error level of the population mean. Generally, constituents could be placed into three groups by sample size (number of samples): 1-50, 51-150, and >150. Aluminum, Ca, Cl, Fe, Mg, Si, SO_4 , electrical conductance (EC), oxidation-reduction potential (Eh) and pH usually required less than 50 samples to be collected for the sample mean to be within 10% of the population mean at a 95% confidence level; B, Co, Cu, K, and V required more than 150 samples.

The number of samples required to minimize variance or costs was determined by using an optimal allocation of resources approach. The sample variance for each constituent was partitioned into the variance due to sampling location, depth zone, and sampling error. This allows the variances to be used as a guide for determining sample sizes for other gob piles without the stipulation that the sampling scheme be identical to that used in this study. Equations were derived to estimate the population variance and costs in collecting samples. Fixing the cost equation, the number of sampling locations and depths per location could be calculated to minimize the variances. Conversely, the variance equation was fixed and the number of samples required to minimize the cost was calculated. Using the variances reported in this study and modifying the cost function to reflect an investigator's costs and precision requirements, estimates of sample numbers can be calculated for other leaching studies where gob pile material is used.

INTRODUCTION

The cleaning of coal is an important part of the coal mining industry. Impurities associated with coal or introduced as a consequence of the mining process are removed by cleaning, which provides a more marketable product. Coal refuse generated from the cleaning process is usually composed of two waste types, gob and slurry, which differ in physical characteristics and methods of disposal.

Gob consists of coarse particles, usually greater than 20 mesh, that are denser than coal and are separated from coal in the cleaning process by gravity and usually disposed of in large piles. Gob contains varying percentages of coal, shale, and other rock, depending upon the coal seam mined as well as the methods of mining and coal preparation. A comparison of gob generated from the mining of bituminous coal with an "average" shale indicated similar chemical composition if the carbon in the gob were excluded. Gob typically contains more sulfur and aluminum and less silica and alkaline earths than an average shale, but overall, evaluation indicates that gob and shale have similar chemical characteristics (Buttermore, Simcoe, and Maloy, 1978).

Slurry, unlike gob, consists of smaller particles that are disposed in a pumpable slurry form and allowed to settle in lagoons. Slurry is usually chemically similar to gob, but has greater carbon and Btu content.

Large quantities of wastes are generated by the coal cleaning process. During 1981, 815 million tons of coal were produced in the United States (Illinois Coal Association, 1983). If cleaning efficiency is estimated to be 85% (i.e., that 15% of the raw coal was disposed of as waste), 122 million tons of coal cleaning wastes were produced in the United States during 1981. In 1981, Illinois mines produced approximately 8 million tons of coal refuse. To date, Illinois has approximately 2,146 and 1,619 hectares (5,300 and 4,000 acres) of land used as disposal areas for gob and slurry refuse, respectively (Nawrot et al., 1982). These coal refuse areas are sources of air and water pollution and detract from the appearance of the surrounding landscape.

Investigators, including Griffin et al., (1980), Roy et al. (in press), Haynes and Klimstra (1975), Buttermore, Simcoe, and Maloy (1978), and others, have chemically characterized coal cleaning wastes. However, little work has been done to determine the variability of chemical constituents in gob piles. An estimate of the variability of constituents is necessary to develop a sampling plan with a known degree of representativeness. Proper sampling is essential if the environmental impact, potential for energy resources, and reclamation of the coal refuse areas are to be assessed accurately. In studying methods for collecting gross coal samples, Aresco and Orning (1965) found that 80% of the total random error variance is normally attributable to sampling, about 15% to sample preparation and less than 5% to laboratory analysis. This indicates that sampling is the largest single source of error.

Maneval (1977) suggested that a gob pile is heterogeneous rather than homogeneous in composition and that variation will occur, both horizontally and vertically, although he did not provide data to support his statements. The variability of material in a gob pile is a function of many factors, including changing efficiencies of the cleaning process, mining methods, and

quality of the coal seam. Maneval concluded that extensive sampling on the surface and at depth must be completed before accurate estimates of the recoverable Btu content of a gob pile can be made.

Eggert, Miller, and Erwin (1980) stated that the distribution of coal within gob piles is largely random, but did not present data to support the claim. They found that sediment distribution within slurry or tailing ponds was not random because deposition of particles was governed by the laws of gravity and settling velocities of moving fluids. Through auger samples, they determined distinct lateral and vertical trends of the sediments in the pond. Materials with high ash and sulfur and low caloric values were found where the slurry entered the pond; materials decreased in sulfur and had high caloric values farther from the slurry discharge point. Caloric values, particle sizes, and sulfur contents of the distal auger samples were vertically stratified. Because gob piles are deposited by different methods than slurry, the factors affecting slurry distribution do not directly pertain to gob piles. The Eggert study demonstrated the need to determine whether gob piles have vertical and lateral stratification of soluble chemical constituents as well as Btu, ash, and sulfur.

There currently are no regulations concerning the handling of abandoned coal refuse either at the federal or state levels. The Surface Mining Control and Reclamation Act of 1977 (SMCRA) was enacted to prevent possible hazards to the environment from coal mining by establishing procedures for disposal of coal wastes from mining and preparation processes. SMCRA provides for the allocation of funds for reclamation of abandoned mined lands that present a hazard to the environment, but does not establish procedures for determining whether a site presents a hazard to the environment. This responsibility may be governed by the provisions of the Clean Water Act of 1977 or the Resource Conservation and Recovery Act of 1976 (RCRA). The Clean Water Act does not address effluents from abandoned coal waste piles or mines. Coal refuse could, however, be potentially classified as a hazardous waste under guidelines developed by RCRA.

Many laboratory leaching methods, such as the EPA extraction procedure and the ASTM water or acid shake extraction procedures have been proposed to assess the potential environmental hazard posed by constituents being leached from a solid waste. Studies that used these leaching procedures (Griffin et al., 1980; Roy et al., in press) have demonstrated that gob leachates exhibit potential corrosivity and have concentrations of constituents that are toxic to plants and fish. According to RCRA, all of these leachate characteristics are criteria for listing a solid waste or its leachate as a hazardous waste.

To accurately evaluate gob piles, it is necessary to develop procedures that will enable procurement of samples of gob that statistically represent the variability of the refuse materials in the piles. Determining the variability that can be expected from the soluble components of the refuse material is the first step in devising such a procedure for collection of gob samples.

PURPOSE AND EXPERIMENTAL DESIGN

The purpose of this study was to investigate the variability of concentrations of water soluble components extracted from solid samples of two abandoned gob piles. The American Society for Testing and Materials Method A water shake extraction procedure (ASTM-A shake test; ASTM, 1979a) was used in this study. From the results, guidelines were developed for the collection of samples to be used in other leaching studies of gob piles.

Two coal refuse sites in western Illinois were chosen for this study. Auger cuttings and split-spoon samples were collected from holes drilled at randomly selected intersections of a rectangular grid superimposed on each site. Standard techniques were used to collect split-spoon samples at discrete depth intervals throughout the gob piles. The split-spoon samples were then subjected to the ASTM-A shake test procedure. Selected split-spoon samples underwent solid analyses to determine Btu and sulfur content as well as other constituent concentrations in the solid samples. Concentrations for 26 chemical constituents as well as pH, EC (electrical conductance), and Eh (oxidation-reduction potential) were determined for each shake test extract. The results of the shake tests underwent statistical evaluation to determine the variability of constituent concentrations, trends in constituent concentrations related to sampling depth and location, and the number of samples required to estimate population means within a defined error or cost.

CONCLUSIONS

Collection of representative gob pile samples to be used in leachate generation studies can be a difficult and somewhat complex task. Each gob pile has its own physical and chemical characteristics that must be considered when planning a sampling protocol. The selection of the parameters to be determined, allowable errors, and confidence limits must be tailored to the hypothesis in question and reflected in the sampling plan.

Constituent concentrations in the ASTM-A shake test extracts compared favorably with those of field- and laboratory-produced leachates reported in the literature (Schuller, Krapac, and Griffin, 1981), indicating that the ASTM-A test may simulate the conditions of field environments. The pH values of extracts ranged from 1.55 to 5.04. On the basis of a comparison between the amount of each constituent in the solid and the concentrations of the constituents in the extracts (on a weight percent basis), the most soluble constituents in the solid waste were found to be Co, Ni, Mn, Ca, and Zn. However, among all the constituents in the extracts, Al, Ca, Fe, SO_4 , and Zn commonly showed the highest absolute concentrations.

Preliminary evaluation of the extract data showed that for most constituents the mean concentration of a constituent for all samples from a drill hole was positively correlated with the variance. That is, when the mean concentrations and variances of a constituent were compared among all drill holes, those with higher mean concentrations also had larger variances. The statistical procedures used in this study require that means and variances of distributions not be related. The means and variances of the common logarithms of constituent concentrations usually fulfilled this independence requirement.

The variation of constituent concentrations in the extracts generated by replication of the preparation, extraction, and analysis of the same sample was small; in most cases coefficients of variation were less than 5%. The within-sample variance for most constituents contributed less than 5% to the total variances of extract concentrations generated by samples collected at different depths and locations. Arsenic, B, Co, K, and V exhibited the greatest within-sample variances; their coefficients of variation were greater than 25%. The large variation for these constituents can be attributed largely to lack of analytical precision. Many of the measured concentrations were close to the detection limits of the inductively coupled argon plasma spectrophotometer (ICAP) used for analysis in this study. Because the within-sample variance constituted such a small part of the total variance, use of only one replicate (one shake test extract) per split-spoon sample was considered representative of these samples.

Several constituents in the extracts and the solid samples exhibited strong relationships ($|r| > 0.70$) between their concentrations and the sample collection depth and between each other. These relationships could allow for the grouping of constituents by ratio estimators.

Results of the general linear model (GLM) procedure, in which the Little Dog extract data were grouped into five depth zones, indicated that all 24 extract constituent concentrations were significantly different due to sampling location (hole). All but four constituents (Be, Cd, K, and Si) were significantly different in relation to sampling depth. The Tukey-Kramer test indicated that the first depth zone (0 to 1.5 m) grouped separately from the other four zones for Al, Ca, Cl, Cr, EC, Fe, Mg, Mn, Na, Ni, pH, SO_4 , TOC (total organic carbon), and V. The top and bottom depth zones (0 to 1.5 m and >9.5 m) were equal and significantly different from the middle depth zones (1.6 to 9.5 m) for B, Ba, and Co.

Superior Washer data showed fewer differences due to sampling location and depth. As, Ca, Cd, Cl, Cu, Eh, Fe, pH, and V showed no significant difference due to sampling location; Al, As, Ba, Ca, Cd, Cr, Eh, Fe, Mn, SO_4 , and V were not significantly different in relation to sampling depth. Of those constituents significantly different due to depth, B, Cu, Ni, and Si were found in the top depth zone (0 to 1.5 m) at different concentrations than the middle and bottom zones (1.6 to >3.4 m); Cl, EC, K, pH, and Zn grouped in the bottom zone differently than in the top and middle zones.

Comparison of mean constituent concentrations between the two study sites showed that only Al, B, Si, and SO_4 in the extracts could be considered statistically equal at the 95% confidence level. Mean concentrations of all other constituents were considered statistically different. There were also differences in levels of variation between sites. Although many of these differences in variation were not statistically significant, they were reflected in the sample numbers needed to achieve a degree of representativeness between the sample and the entire gob pile. These results indicated that each gob pile must be treated individually when developing a sampling plan. One must remember that these findings were based on only two gob piles; when more gob piles are investigated, similarities between piles may be found.

The pattern of variation between sites with respect to hole location and depth suggests that, in general, gob piles are not homogeneous and cannot be represented by a simple sampling method. The sampling design used to investigate gob pile characteristics must be carefully tailored to the study hypothesis.

The number of samples necessary to achieve a given variance within a particular cost constraint may be determined through an approach that utilizes an optimal allocation of resources. By partitioning the sample variances for each constituent into variances resulting from sampling location (hole), depth, and error, the variances can be used as a guide for determining sample sizes for other gob piles (assuming similar levels of variance) without the stipulation that the sampling scheme be identical to that used in this study. Equations for estimating the population variance of a particular constituent and the cost of collecting and analyzing samples were used to develop computer programs that determined the number of samples required to minimize cost for a fixed variance or to minimize variances for a fixed cost.

RECOMMENDATIONS

A detailed sampling plan should be developed to ensure that the objectives under investigation can be achieved. The principal steps in developing a sampling plan are: 1) identification of the goals for the study, i.e., what hypotheses are being tested, 2) identification of the type of data relevant to the goals of the study, 3) identification of the population to be sampled, 4) specification of the degree of precision of the results - samples are always subject to some uncertainty because only part of the population has been measured and errors occur in measurements, 5) selection of the sample - because only a portion of the population is being sampled, the sample must cover the whole of the population and not overlap, 6) selection of the sample sizes - a variety of sampling strategies are available; for each strategy, estimates of the number of samples to be collected can be made from a knowledge of the degree of precision desired, and 7) identification of statistical methods for summarizing and forming inferences from the data generated by the sample.

On the basis of this study, the following recommendations are made for the collection of coal refuse samples for leachate generation studies:

1) Variations in constituent concentrations in laboratory produced extracts are related to sampling depth; this suggests that samples should be collected at various depths in the pile.

2) If only the mean concentration for a particular constituent is of interest in a pile, then a continuous core sample could be collected from each sampling location.

3) If concentration trends due to sample depth are of interest, samples should be collected equidistant from each other and at similar sampling depths so that the statistical models used to evaluate the data will be free of empty data cells and sample sizes at various depths will be similar.

4) Sample location was found to have an effect on constituent concentrations in the extracts, which implies that samples should be collected from various sampling locations on the gob pile. Many sampling strategies are available; however, we suggest for statistical validity that a random or a stratified sampling plan be used. Generally, samples should be collected from the periphery as well as the center of the gob pile.

5) Constraints due to time, finances, etc. may limit sampling to one collection period. If a single sampling plan is implemented, and the

variability of the constituent in the gob pile under study is unknown, the number of samples required to achieve a defined degree of precision may be difficult to estimate. The sample sizes, methods, and variances given in this report may be used as a guide for collecting an adequate number of samples.

6) If the sample sizes listed in this report are used in other studies, the relatively large number of samples required to have the sample mean within a defined error level of the population mean for some extract constituents may prohibit all the samples from being analyzed. We suggest that all the samples be collected but only between 5 and 30 samples be analyzed initially. From these results a sample mean and variance can be determined. The various methods listed in this report can then be used to estimate the number of samples required to achieve a certain precision, cost, or variance.

7) A tiered sampling plan involving a pretest may increase precision of the sample data. The pretest may reveal problem areas and allow improvement of the initial sampling plan. A pretest includes collection and analysis of approximately 30 samples; a sample size for the precision level desired is calculated from the mean and variance of the pretest sample. The collection of 30 samples is somewhat arbitrary but, on the basis of the Central Limit Theorem of statistics, sample sizes greater than 30 are more likely to be normally distributed. This allows the use of certain statistical techniques. Once the sample size has been calculated from the pretest sample, further samples are then collected, if necessary, to fulfill the precision requirements established in the sampling plan.

SITE DESCRIPTION

Fifteen gob sites were considered for possible use in this study. The Little Dog Mine and Superior Washer sites near the town of Gillespie, Macoupin County, in southwestern Illinois were selected. The criteria for determining site selection were: 1) size - a gob pile ranging from 4 to 20 hectares (10 to 50 acres) was felt to be manageable within the time constraints of the study; 2) accessibility - the site had to be accessible by a portable drilling rig; 3) ownership - the owner of the site had to be known in order to obtain permission to collect samples.

The Superior Washer site is located in Macoupin County, Section 17, T. 8N., R. 6W., approximately 1.6 kilometers east of the town of Gillespie. Between 1937 and 1950 the Washer site received Herrin (No. 6) Coal from four deep mines (labelled S#1, S#2, S#3, and S#4 in fig. 1) for cleaning and shipping.

The Superior Washer site covers roughly 22 hectares (54 acres). The site is a low flat plateau, but has large gullies and a conical pile of gob approximately 9.2 m (30 ft) tall in the center of the site. Two intermittent tributaries of Spring Creek drain the site along the eastern side of the property. Railroad tracks, a farm field, and a county road run along the western, northern, and southern edges of the property, respectively.

The southern one-third of the property has been used as a dump for tree trimmings, household refuse, and construction materials. The boundaries of the area studied were restricted to the northern two-thirds and are defined by the railroad tracks to the west, the farm field to the north, the drainage ditch to the east, and the large gob pile and the erosion gullies beside it to the south.

The coal refuse at the Superior Washer study area ranges in thickness from 3.0 m to 6.7 m (10 ft to 22 ft). A layer of gob consisting of coal, pyritized fusions, shale, and clay overlies a layer of slurry. The gob layer varies in thickness from 1.5 m to 4.6 m (5 ft to 15 ft). The slurry is approximately 1.5 m (5 ft) thick and also contains coal, shale, clay, and pyrite.

The Little Dog site is located in Macoupin County, in Section 13, T. 8N., R. 7W., approximately 0.4 kilometers north of the town of Gillespie (fig. 1). The Little Dog Mine was in operation from 1919 to 1968. During this period a total of 1.16×10^{10} kg (1.28×10^7 tons) of Herrin (No. 6) Coal was mined and cleaned.

The Little Dog site occupies roughly 20.9 hectares (51 acres), of which 4.0 hectares (9.8 acres) are gob, 4.0 hectares are slurry, 4.3 hectares (10.6 acres) are tipple, and 8.6 hectares (21.2 acres) are off-site areas affected by the wastes. Visual inspection of the site shows three distinct areas: 1) a pile approximately 12.2 m (40 ft) tall, composed of gob and slurry and located at the southeast corner of the property; 2) a slurry pond located at the northeast corner of the property and; 3) a gob pile - the object of our

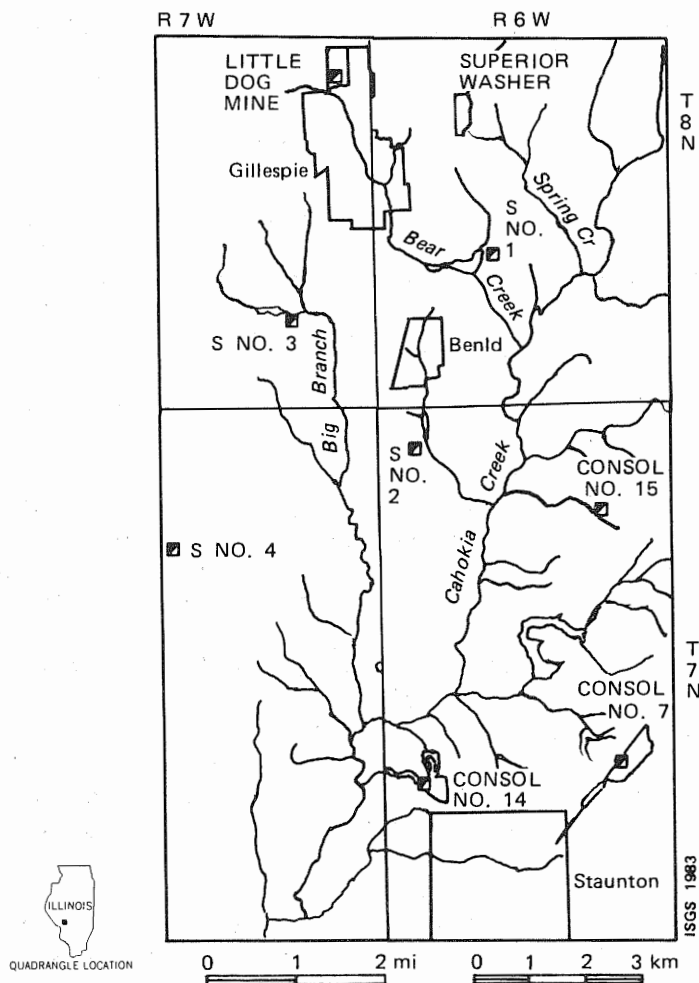


Figure 1. Location of the Little Dog and Superior Washer gob piles.

study - located at the northwest corner of the property. The Little Dog site is drained to the north and west by two intermittent drainage ditches that enter a small stream located along the eastern edge of the property. This stream flows through the town of Gillespie and enters Bear Creek, a tributary of Cahokia Creek.

The Little Dog site is bounded by an abandoned railroad line to the west, a farm field to the north, a drainage ditch to the east, and houses to the southwest. The gob pile in the northwest corner of the property was chosen as the study area. The pile ranges in height from 3.0 m to 13.7 m (10 ft to 45 ft). This area is bounded by the abandoned rail line and farm field to the west and north, respectively. The slurry pond forms the eastern boundary; the slurry pond retaining wall and a large gully form the southern boundary.

PROCEDURES

Grid pattern and mapping

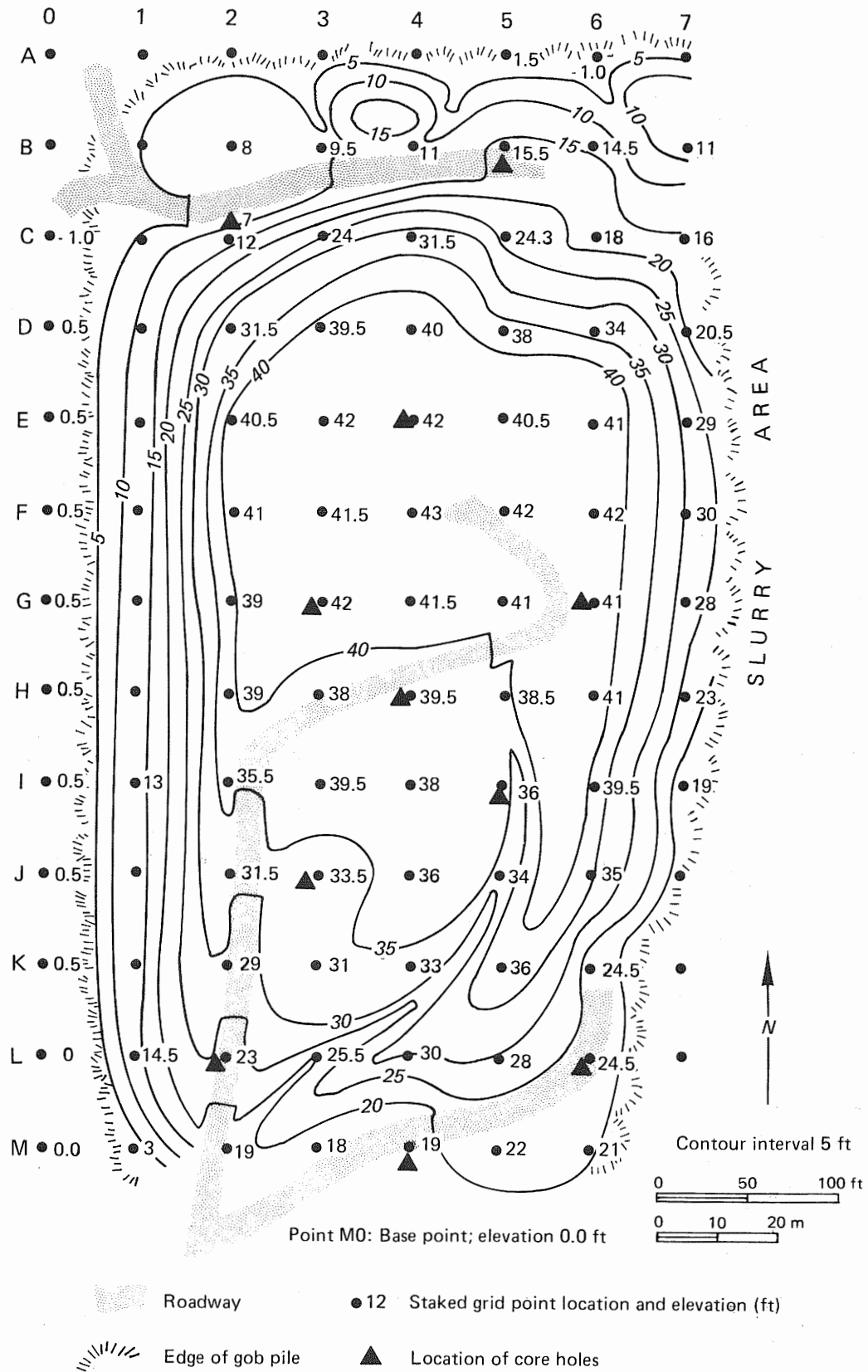
Aerial photographs, 7.5 minute quadrangle maps, and visual inspection of the sites were used to determine the dimensions of the study areas. The Little Dog study area is 158 m long by 96 m wide by 12 m high (520 ft by 315 ft by 40 ft). The Superior Washer study area is 380 m long by 350 m wide by 6 m high (1250 ft by 1156 ft by 20 ft).

A grid system, enabling a random selection of sampling points, was established at each of the study areas. Aerial photographs were used to orient the grid, determine grid point spacings, and to select a base station from which to lay the grid. A 50.3 m (165 ft) long measuring tape and magnetic compass were used to make intersecting north-south and east-west traverses from the base station at each study area. Stakes were driven at 15.2 m (50 ft) intervals along the traverses at the Little Dog site and at 38.1 m (125 ft) intervals at the Superior Washer site. At each area the remaining portions of the grid were measured from the base station and the traverses. Grid point locations were checked periodically with the compass. Seventy and 85 grid points were plotted at the Little Dog and Superior Washer sites, respectively. A coordinate system allowing identification of each grid point by a number-letter pair was adopted. A random drawing using the number-letter pairs was used to determine which grid points would be used as sampling sites.

Topographic maps

Topographic surveying at each site was done with a hand level, leveling rod, and aerial photos that used the grid point stakes as references. Readings were made to the nearest 0.15 m (0.5 ft) and the accuracy of the elevations of any point was 0.3 m (1 ft). Contour maps of each site are in 1.5 m (5 ft) contour intervals.

The topographic maps of the Little Dog and Superior Washer sites are shown in figures 2 and 3, respectively. Datum points, M0 and I0 (native soil surface) were selected at the Little Dog and Superior Washer sites, respectively, and assigned an elevation of 0.0 feet. The elevations used to construct each map are in relation to this point instead of mean sea level because we were interested in the size and shape of the piles relative to the normal, nearly horizontal soil surface at the respective sites. The locations of stakes marking the grid intersections and their corresponding elevations



ISGS 1982

Figure 2. Contour map of the Little Dog gob pile study area.

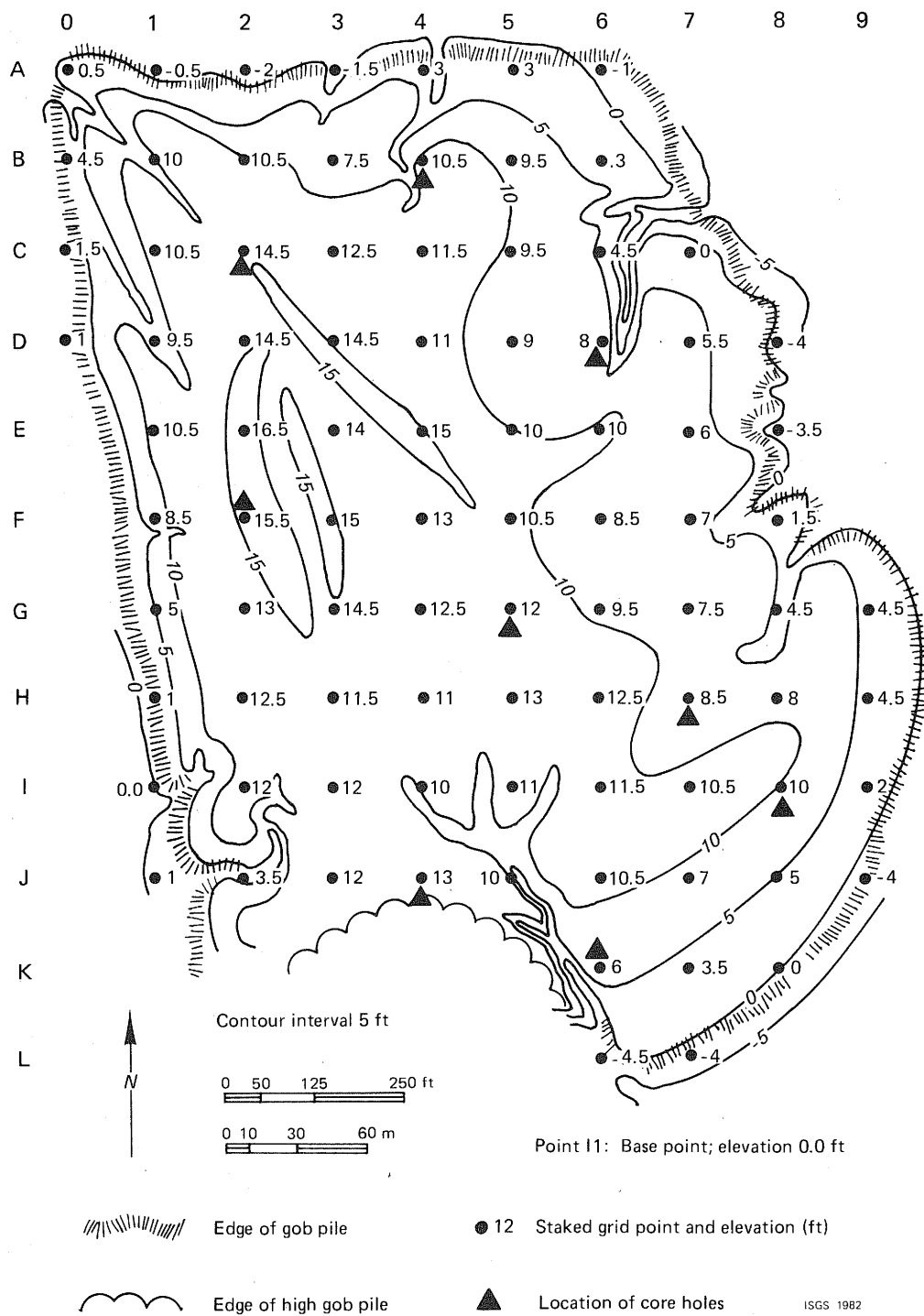


Figure 3. Contour map of the Superior Washer gob pile study area.

are noted on the map. Sampling locations and the access roads to the pile are also indicated on the maps.

Sampling

Determining the variability of chemical constituents in the gob piles required that split-spoon samples be collected at various depths and locations in the piles. A Mobile® B30-S, trailer-mounted drilling rig was used to collect split-spoon and auger cutting samples. Steep slopes and gullies interfered with the access of heavy equipment to the gob piles; in some instances, roads had to be constructed to grid point locations.

A standard engineering split-spoon sampler was used to collect core samples at discrete 0.6 m (2 ft) intervals. The sampler consisted of a 0.6 m (2 ft) long by 5.1 cm (2 in.) OD thick walled steel tube that had been cut in half lengthwise and threaded at both ends. A blunt edged nose piece with a sample catcher was attached to the down-hole end of the sampler. The split-spoon assembly was attached to 1.5 m (5 ft) lengths of "A" rod and lowered through the center of a hollow stem auger. A 64 kg (140 lb) hammer and pulley assembly was then used to drive the split spoon 0.6 m (2 ft) below the point where augering ceased. The split spoon was then retrieved from inside the auger. A core sample 4.4 cm in diameter was removed from the split spoon. Augering then continued to the top of the next 0.6 m sampling interval and the procedure repeated. Sampling continued until the sampler penetrated the loess soil of the original land surface.

A composite was made of each 0.6 m split-spoon sample and placed in plastic bags and sealed. Sample size was dependent upon the amount of material recovered by the split spoon and ranged from 50 g to 1000 g. Due to the small size of the split-spoon samples, supplemental auger-cutting samples were collected at depths less than 6.1 m (20 ft). These samples corresponded to the material taken by the auger as it passed through the interval sampled by the split spoon. Each auger sample weighed approximately 1500 g. Although split-spoon samples were collected to depths of 14.3 m (47 ft), auger-cutting samples were only collected to about 6.1 m (20 ft). Below six meters, auger samples were too contaminated by gob caving off the sides of the hole to be as reliable in producing samples from the same depth intervals as the split-spoon samples.

Nine holes were drilled at the Superior Washer site; figure 3 shows hole locations. The holes ranged in depth from 4.3 m to 6.1 m (14 ft to 20 ft). All nine holes were sampled at 0.6 m increments for the entire depth drilled. Seventy-five split-spoon and 57 auger samples were collected from these nine holes.

Eleven holes drilled at the Little Dog site yielded 125 split-spoon and 98 auger samples; figure 2 shows hole locations. These holes ranged in depth from 3.7 m to 14.3 m (12 ft to 47 ft). The entire depth of three of the holes was sampled at 0.6 m increments. The remaining eight holes were continuously sampled to a depth of 3.7 m (12 ft); after this point samples were collected at 1.5 m (5 ft) intervals.

Sample preparation

Sample preparation of the 355 samples involved: 1) air drying the sample; 2) reducing the samples to pass through a U.S. Standard Number 4 (4.76 mm) mesh sieve; 3) splitting each sample to obtain two representative subsamples; 4) grinding one of the subsamples to pass through a U.S. Standard Number 60 (.250 mm) mesh sieve; and 5) splitting this 60 mesh sample to produce two equally sized subsamples. In this paper the term sample, unless otherwise specified, will refer to the split-spoon sample material.

To ensure that they would properly feed through the crushing and dividing equipment, samples were air dried. Samples were piled on paper plates to a depth not greater than 4 cm and periodically stirred to hasten drying. Drying time, which ranged from 24 to 48 hours, was kept to a minimum to prevent excessive oxidation of the solid. A sample was deemed "dry" when it felt dry to the touch and crumbled easily.

Each sample was crushed through a large jaw crusher until at least 95% (by weight) of the sample passed through a No. 4 mesh sieve. The <4-mesh sample was divided through a riffle until two subsamples that weighed 125 g and 85 g, respectively, were obtained.

The ASTM-A shake tests used the 125 g subsamples. Samples for solid analysis (85 g) were further ground with a Holmes® grinder to pass a No. 60 mesh sieve and divided with a microriffle into two equal aliquots for analysis of inorganic constituents and Btu content.

To determine any variance introduced by grinding, splitting, and analysis procedures, six auger samples were randomly selected and prepared as outlined above. Each of the six samples were subsampled until ten of each of the 125 g and 85 g sample sizes were obtained. Ten shake tests were performed for each auger sample.

Solid analysis of split-spoon samples

Chemical determinations for the approximately 25 inorganic constituents were made for 32 split-spoon solid samples. Instrumental neutron activation, optical emission spectrochemical analysis, atomic absorption spectrometry, x-ray fluorescence, and ion-selective electrode methods were used to determine the concentration of constituents in the solid samples. Except for those constituents determined by atomic absorption, the solid samples were air dried. The samples analyzed by atomic absorption were submitted to low temperature ashing and subsequent dissolution. A detailed discussion of procedures for analyses of chemical constituents in solid samples is given in Harvey et al. (1983). National Bureau of Standards coal samples and U. S. Geological Survey rock samples were analyzed for a quality assurance program to determine the accuracy, reproducibility, and precision of the analytical methods employed.

Additional analyses were conducted to determine the percentage of pyritic, sulfate, and organic sulfur in 59 solid samples. The sulfate-sulfur and pyritic-sulfur concentrations in the solid samples were determined by the ASTM D-2492, varieties of sulfur procedure; total sulfur was determined by the ASTM D-3177, Eschka method. The organic sulfur concentration was that quantity of the total sulfur unaccounted for by the sulfate and pyritic sulfur. Btu content of the 59 solid samples was determined by a rapid automated calorimetric method (Parr Model 1241, Model 1680 Master Control).

Shake tests

The ASTM-A shake test is intended to be a rapid means of obtaining a solution for evaluation of the water extractable materials in a waste from a solid sample. The procedure consists of making a 25% slurry (solid wt/liquid vol). The slurry is shaken for 48 hours, then the extract is filtered and analyzed (ASTM, 1979a).

The ASTM shake test procedure was slightly modified to accommodate the smaller sample size that resulted from the split-spoon sampling technique. Instead of the recommended 700 g sample weight, 100 g of sample were used. The procedure also recommends using the waste material in the physical form in which it was disposed. This recommendation was impractical for the coal refuse material being studied because the extreme variability of particle size (clay to boulder) and the sampling techniques used (split-spoon) made subsampling in that form impossible. An increment sampling process was employed in which the split-spoon sampler was considered analogous to a cross-stream cutter at a randomly selected point in the grid. The ASTM procedure (D-2013) for preparing coal samples, in which the samples were ground to pass a No. 4 mesh sieve, was therefore employed (ASTM, 1979b).

The ASTM procedure involved shaking a slurry composed of $100 \pm .01$ g of waste with a volume of deionized water equal in milliliters to four times the weight in grams of the sample. The slurries were made in 500 mL wide-mouth glass bottles that were sealed with teflon lined plastic lids and shaken at room temperature for 48 hours on a reciprocating platform shaker operated at 60 to 70 1-inch strokes per minute. The slurries were allowed to settle for 1 hour after shaking; oxidation-reduction potential (Eh), pH, and specific conductance (EC) were measured immediately after opening each bottle. The slurries were then decanted and the supernate filtered through Millipore® 0.45 μ m pore size cellulose acetate membrane filters. Three subsamples of the filtrate were taken for cation, anion, and total organic carbon (TOC) analysis.

Shake test extracts

A total of 260 shake tests using the ASTM-A shake test procedure were completed. One hundred twenty-seven shake tests were generated by the Little Dog and 73 by the Superior Washer split-spoon samples. Sixty shake tests were performed on auger samples from both sites to determine the variability of the sample preparation and shake test procedures.

A Jarell-Ash Model 975 inductively coupled argon plasma spectrometer (ICAP; Jarell-Ash Division, 1978) was used to analyze the Al, As, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sn, V, and Zn concentrations of the extracts generated by the shake test procedure. Sulfate (SO_4) was measured turbidimetrically and chloride (Cl), oxidation-reduction potential (Eh), pH, and electrical conductance (EC) were measured by electrodes (American Public Health Association, 1975). A Beckman® Instruments Tocamaster 915B total organic carbon (TOC) analyzer was used to determine the TOC content of the aqueous extracts.

Reference waste-water samples obtained from Environmental Resources Associates and the U.S. EPA Quality Assurance Branch were used to check the reproducibility and accuracy of the analytical methods used in this study. The ICAP results were within 5% of the true value listed for the quality control samples. Extract solutions were diluted to check for spectral inter-

ferences and the necessary actions were taken to correct any interferences. Typical ICAP detection limits are given in appendix A. For further information pertaining to ICAP detection limits, accuracy, reproducibility, and interferences, refer to the U.S. EPA method 200.7 (U.S. EPA, 1980a).

Statistical analyses

Results of analysis of the extracts underwent summary as well as inferential statistics. Due to the complexities of some of the statistical procedures, a brief discussion of each procedure and the justification for its use is given in each subsection of the "Statistical results of the extract data" section of this report. In general, the routines in the 79.6 version of the Statistical Analysis System (SAS, 1979) computer program on an IBM 4341 computer of the University of Illinois, Urbana-Champaign campus were used to store and retrieve data, and to determine all summary and analysis of variance statistics. An adaptation of the Semi-Variogram Estimation and Universal Krieger computer program, developed by the U. S. Geological Survey (Skrivan and Karlinger, 1980) and run on a CDC Cyber 175 computer at the University of Illinois, was used to determine all variogram results. Other computer programs for compilation of suggested sample sizes, finite population corrections, and miscellaneous calculations were written by the authors.

CHARACTERIZATION OF SOLID SAMPLES

Little Dog split-spoon samples

Sixteen split-spoon samples collected at various depths from the Little Dog site underwent chemical analyses; an additional 15 samples (31 samples total) were analyzed for total sulfur, ash, and caloric content. SiO_2 , Fe_2O_3 , Al_2O_3 and S (sulfur) were the most prevalent constituents; they compose approximately 61% of the solid sample. The most abundant trace elements in the solid were B, Ba, Sr, and Zn. A summary of constituent concentrations is in table 1. Caloric contents on a moisture-free basis ranged from 730 to 6,949 Btu/lb. A confidence interval to estimate the population Btu mean (the average caloric content of the gob in the entire pile) at a 95% confidence level was calculated from the sample mean and standard deviation and was found to be $3,550 \pm 531$ Btu/lb. Analysis of variance results indicated that caloric content (Btu) of solid samples collected at various depths and locations in the refuse pile was equal, which implies that the caloric content of the coal refuse material was independent of sample depth and location. Sulfur contents of the material ranged from 2.52 to 21.4%, and the mean was 11.2%. No apparent trends related to sampling depth were observed.

The following equation was used to estimate the number of split-spoon samples required to ensure that the sample mean for caloric content (Btu) would fall within a given percent error of the population mean (see "Determination of sample sizes using a t distribution," p. 43, for more information).

$$n = \left[\frac{t_{(\alpha/2, n-1)} s}{r\bar{x}} \right]^2$$

Table 1. Summary of constituent concentrations in the Little Dog split-spoon samples.

Constituent	Sample Size	CV* (%)	Mean	Standard Deviation	Minimum	Maximum
percent						
SiO ₂	16	15.5	28.0	4.2	19.5	32.3
TiO ₂	16	20.0	0.5	0.1	0.3	0.5
Al ₂ O ₃	16	18.1	8.3	1.5	5.5	10.4
Fe ₂ O ₃	16	46.0	13.9	6.4	4.4	26.9
CaO	16	60.3	1.8	1.1	0.1	3.50
MgO	16	-	-	-	2.0	2.0
Na ₂ O	16	42.9	0.28	0.1	.14	0.57
K ₂ O	16	21.1	1.2	0.3	0.8	1.7
P ₂ O ₅	16	79.7	0.7	0.6	0.1	2.1
Sulfate sulfur	16	46.7	2.12	0.99	0.75	3.70
Pyritic sulfur	16	64.2	7.79	5.00	0.56	19.05
Organic sulfur	16	-	1.14	-	4.51	-
Total sulfur	31	42.8	11.2	4.79	2.52	21.4
High Temp. Ash	31	15.5	61.8	9.6	35.2	86.3
Btu/lb	31	40.8	3,550	1,449	730	6,949
mg/kg						
As	16	40.6	19.7	8.0	3.1	30.0
B	16	45.5	145	66	51	248
Ba	16	15.7	216	34	126	253
Be	16	30.7	1.7	0.5	0.63	2.5
Cd	16	-	-	-	-	-
Co	16	57.3	5.34	3.1	0.8	12.0
Cu	16	97.7	56.3	55.0	9.00	248
Mn	16	52.9	87.4	46.2	11.0	186
Mo	16	53.4	11.6	6.2	2.00	23.0
Ni	16	81.5	27	22	<5	79.0
Pb	16	-	-	-	<3	<22
Sb	16	30.4	1.1	0.3	0.5	4.0
Se	16	66.1	12.4	8.2	7.1	41.0
Sr	16	25.2	107	27	50.5	139
V	16	83.7	84.1	70.4	22.0	330
Zn	16	157	7,006	1,110	5.9	3,580

*coefficient of variation = $\frac{\text{standard deviation}}{\text{mean}} \times 100\%$

where n = number of samples
 s = standard deviation of the Btu values from the 28 or 31 samples analyzed for this study
 \bar{x} = mean Btu value from the 28 or 31 samples analyzed for this study
 r = specified error of the population mean
 t = t statistic, where $\alpha/2 = .025$ at a 95% confidence level.
 If the number of samples is greater than or equal to 30, $t(0.025) \approx 1.96$.

The results of increasing sample size on the estimation of the population mean for Btu are shown in figure 4. The y axis of the graph is the error level (r , in percent) in estimating the population mean for the corresponding sample size (x axis).

The graphs clearly depict that increasing precision from 25% to 5% requires a relatively small increase in the number of samples collected as compared to an increase in precision to the 1% error level. This relationship is not a function or characteristic of the gob samples, but a function of the equation determining the number of samples. From the equation, n is proportional to $1/r^2$ such that a change in r from 25% to 5% requires an increase in the number of samples by a factor of 25; however, a change in r from 25% to 1% requires an increase in the sample number by a factor of 625. Collection of approximately 50 samples would probably provide the most accurate estimate for the Btu content of the gob pile ($\pm 10\%$ error) for the least amount of effort, analyses, and expense.

Because of its relatively low caloric and high sulfur content, this gob material is an unlikely primary energy source at the present time. However, certain methods of processing the gob (such as crushing and washing to remove sulfur and ash-forming constituents, or blending the refuse with coal) might

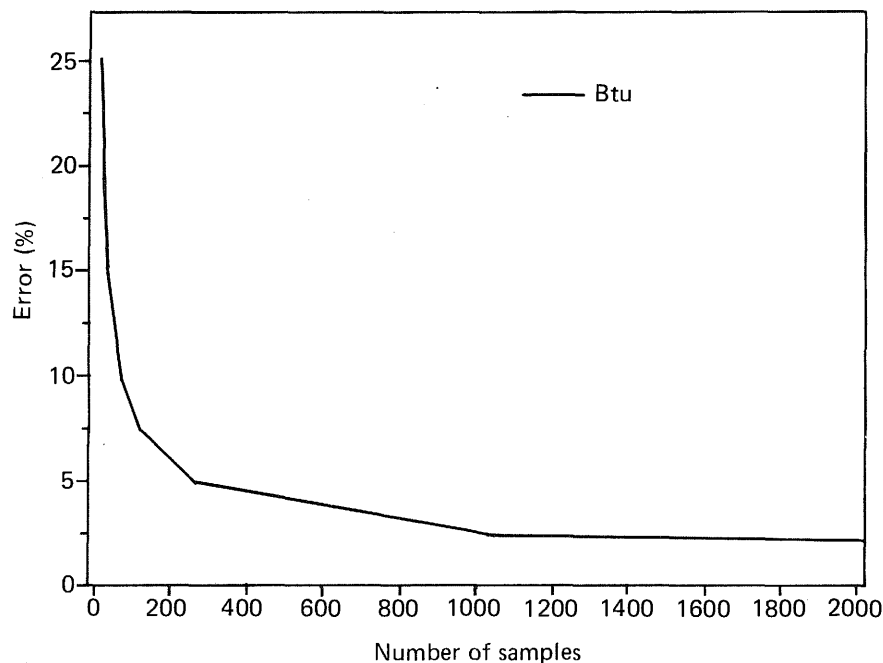


Figure 4. Effects of number of samples collected relative to percent error in estimating Btu population mean at the Little Dog site.

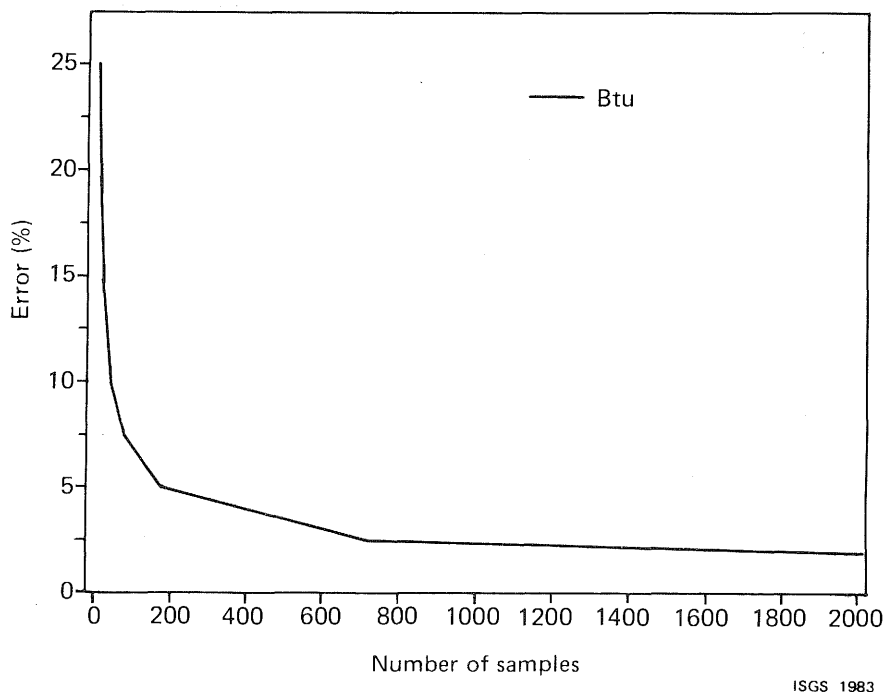
make the gob material a more plausible energy source. Because the gob material is in piles on the ground, many of the costs associated with mining coal in the ground have been eliminated.

Superior Washer split-spoon samples

Chemical analyses for major and trace elements in the solid sample material were performed on 16 split-spoon samples collected from the Superior Washer site; 28 samples underwent total sulfur, ash, and caloric content determinations. Table 2 summarizes the results of these analyses. The mean caloric content (6,334 Btu/lb) of the Superior Washer samples was greater than that of the Little Dog samples, and also exhibited greater variability (2,339 Btu/lb to 10,445 Btu/lb). This variability might be caused by the two different kinds of coal preparation waste which form the deposit. The slurry underlying the gob had a higher Btu and lower sulfur and ash content than did the gob. The gob and slurry samples had a mean caloric content of 5,193 Btu/lb and 8,749 Btu/lb, respectively. The combined sample means and standard deviations were used to calculate the mean caloric content of the gob in the entire pile at a 95% confidence interval ($6,334 \pm 833$ Btu/lb).

Chemical composition of the Superior Washer solid samples was similar to that of the Little Dog samples. The major differences between the two sets of samples were that Cd, Cu, Mn, and Zn concentrations were between two and ten times greater in the Little Dog samples. These differences also were reflected in the ASTM extracts, in which the Little Dog extracts exhibited greater concentrations of the above constituents.

Figure 5 shows the effect of increasing sample size on the precision of estimating the population Btu mean. The results are similar to those of the Little Dog site and show an inflection point at the 5% error level. As previ-



ISGS 1983

Figure 5. Effects of number of samples collected relative to percent error in estimating Btu population mean at the Superior Washer site.

Table 2. Summary of constituent concentrations in the Superior Washer split-spoon samples.

Constituent	Sample size	CV* (%)	Mean	Standard Deviation	Minimum	Maximum
percent						
SiO ₂	16	21.4	26.6	5.7	17.1	40.4
TiO ₂	16	20.0	0.5	0.1	0.3	0.7
Al ₂ O ₃	16	22.6	8.4	1.9	5.1	13.2
Fe ₂ O ₃	16	53.0	7.4	3.9	3.2	17.9
CaO	16	82.5	1.8	1.5	0.4	7.0
MgO	16	-	2.0	-	2.0	2.0
Na ₂ O	16	40.0	0.20	0.08	0.09	0.39
K ₂ O	16	34.2	1.1	0.4	0.6	2.0
P ₂ O ₅	16	79.1	0.4	0.3	0.1	1.4
Sulfate sulfur	16	51.3	1.89	0.97	0.80	5.12
Pyritic sulfur	16	86.8	3.42	2.97	0.30	11.2
Organic sulfur	16	25.0	1.16	0.29	0.68	1.74
Total sulfur	28	49.0	5.78	2.83	2.68	14.8
High Temp. Ash	28	29.7	44.8	13.3	20.2	70.8
BTU/lb.	28	33.9	6,334	2,148	2,339	10,445
mg/kg						
As	16	18.2	15	2.8	11	22
B	16	61.8	173	107	84	490
Ba	16	24.1	187	45	124	302
Be	16	70.9	1.17	0.83	<1.0	3.0
Cd	16	-	-	-	<0.9	<1.5
Co	16	75.0	3.6	2.7	0.9	9.8
Cu	16	31.3	32	10	14	43
Mn	16	82.6	46	38	15	155
Mo	16	41.7	12	5	2	23
Ni	16	76.5	17	13	<5	36
Pb	16	56.7	-	-	<10	27.0
Sb	16	45.5	1.1	0.5	0.7	2.8
Se	16	52.4	12.6	6.6	6.2	33
Sr	16	25.2	93.9	23.7	56.3	156
V	16	44.1	52	24	27	120
Zn	16	197	75.7	149.2	8.9	592

*coefficient of variation = $\frac{\text{standard deviation}}{\text{mean}} \times 100\%$

ously noted, increasing of number of samples has little effect on increasing precision of the population estimate below the 5% level.

The Superior Washer preparation waste may be a more likely energy source than the Little Dog gob because of its higher caloric and lower sulfur and ash content. The mean sulfur, ash, and Btu contents of Illinois coals are 3.6%, 11%, and 12,712 Btu/lb, respectively (Gluskoter et al., 1977). The waste material has a higher mean sulfur (5.78%) and ash (44.8%) content and lower Btu (6,334) content than most Illinois coal. Most coal-burning power plants operate with coal having fuel values that range between 10,000 and 12,000 Btu/lb and ash contents up to 30%. Processing the gob to meet power plant standards would involve selective processing of the slurry layer or stripping off and discarding the gob layer if coal could not be recovered from it economically. Blending the waste with mined coal may increase the marketability of the material. Materials with low heating values can, however, be burned. Coal refuse crushed to pass a 0.64 cm sieve (1/4 in.) and with as little as 3,000 - 3,500 Btu heating value has been burned in the Energy Research and Development Administration pilot scale fluid-bed column designed and operated by Pope, Evan, and Robbins. On a dry basis, this refuse could contain 65 to 70% ash (Maneval, 1977). The Superior Washer gob may be a primary energy source if specially designed boilers are available.

AN OVERVIEW OF ASTM-A EXTRACTS

Little Dog extracts

The results of 117 ASTM-A extracts were used to describe the characteristics of the water soluble components in the Little Dog split-spoon samples. Table 3 summarizes the constituent concentrations found in the extracts. The extracts have a mean pH value of 2.60; some extracts have pH values as low as 1.55 and as high as 5.04. The constituent concentrations in the extracts ranked: $SO_4 > Fe > Ca > Al > Na > Mg > Zn > Cl > TOC > Si > Mn > Ni > K > Cu > V > B > CO_2 > Cd > As > Cr > Be > Ba$, with Mo, Pb, Sb, Se, and Sn concentrations below detection limits (appendix A). Although similar Na concentrations were found in solids from both sites (tables 1 and 2), the Na concentration in the Little Dog extracts had a mean value of 95.6 mg/L; the Na concentration of the Superior Washer extracts was below detection limits. Closer inspection of the Little Dog Na data indicates that the Na concentrations in extracts generated from split-spoon samples collected between 0.3 m and 3.4 m were less than the detection limit; Na concentrations in the extracts of samples from depths greater than 3.4 m generally ranged between 100 - 300 mg/L. Because Na is a relatively hydrophilic element, this difference in Na concentration in relation to depth may be a good indicator of the weathering or leaching zone in the Little Dog site. The Superior Washer site averages 3.4 m in depth; all the extracts generated by samples collected at various depths within the pile had Na concentrations less than the detection limit. This indicates that the weathering and or leaching processes may be occurring throughout the entire Superior Washer site. Although SO_4 had the greatest concentrations in the extracts, Ni was the most soluble constituent -- 71% of the total nickel in the solid samples was solubilized. On a weight/percent basis, the ranking of the amount of a constituent leached in comparison to the total amount in the solid was: $Ni > Co > Cd > Mn > Na > Ca > Zn > Cu > Be > SO_4 > As > Fe > V > Al > B > K > Si > Ba$.

Table 3. Summary of constituent concentrations (mg/L) in the Little Dog ASTM-A extracts.

Constituent n = 117 ^a	Mean	Standard Deviation	CV ^d (%)	Median	Minimum	Maximum
Al	231	218	94.4	156	3.36	1,035
As	0.25	0.28	112	0.15	<.05	1.39
B	0.58	0.57	98.3	0.50	<.002	3.07
Ba	0.009	0.008	88.9	0.01	<.001	0.03
Be	0.025	0.016	64.0	0.02	<.002	0.09
Ca	478	75	15.7	492	136	692
Cd	0.56	0.96	171	0.31	0.04	7.63
Cl	19.0	16.9	88.9	12.6	<1.0	83.5
Co	0.57	0.53	93.0	0.50	<.01	3.06
Cr	0.25	0.59	236	0.08	<.03	5.05
Cu	1.40	3.50	250	0.60	<.01	26.9
EC ^b	5,675	2,525	445	4,725	2,990	17,000
Eh ^c	618	46	7.4	625	426	712
Fe	951	154	363	5.76	5,607	
K	3.95	4.17	106	2.84	<1.03	18.8
Mg	65.16	34.64	53.1	54.2	8.51	165
Mn	5.69	3.93	69.1	4.87	0.54	21.4
Na	95.6	99.9	104	78.2	<1.42	370
Ni	4.74	5.61	118	3.11	0.18	52.1
pH ^e	2.61	0.58	22.2	2.59	1.55	5.04
Si	8.23	4.75	57.7	7.29	2.35	46.8
SO ₄	4,777	2,934	61.4	3,773	1,950	18,035
TOC ^d	10.03	8.24	82.2	7.52	2.43	66.6
V	0.61	0.68	111	0.38	<.04	4.49
Zn	25.2	39.5	157	11.9	0.48	278

^anumber of samples

^bμmhos/cm

^cmillivolts relative to normal hydrogen electrode

^dcoefficient of variation = $\frac{\text{standard deviation}}{\text{mean}} \times 100\%$

^elog a^{H+}

An initial statistical evaluation of the extract data was performed on nine constituents (Al, Ca, EC, Fe, Mg, pH, SO₄, TOC, Zn). These constituents were selected because they were prevalent in the extracts and they can be used as indicators of environmentally significant chemical processes taking place in gob piles. Extracts from the same sample depth, but from the various sampling locations, were grouped and the averages of the chemical compositions and standard deviations were calculated and are shown in table 4.

The mean concentrations in table 4 were plotted against sample depths to determine whether any trends were visible. Figure 6 indicates that Al, Fe, and SO₄ concentrations in the extracts decreased from 0 to 5.0 m and then assumed relatively constant concentrations at depths greater than 7.5 m. Calcium and Mg concentrations generally were less variable than Al, Fe, and SO₄, and increased or remained constant as depth increased.

Table 4. Sample depth averages and standard deviations of selected constituent concentrations (mg/L) in the Little Dog ASTM-A extracts.

	Depth 0.3m n=11 ^a		Depth 1.5m n=11		Depth 3.4m n=10		Depth 5.0m n=10		Depth 6.4m n=7	
	\bar{x} ^b	S ^c	\bar{x}	S	\bar{x}	S	\bar{x}	S	\bar{x}	S
Al	388	265	438	268	205	196	134	119	126	105
Ca	396	125	468	47	485	70	454	79	499	29
EC ^d	10332	3560	6639	2937	4540	1206	5115	1485	4870	1040
Fe	2119	1384	1365	1651	415	333	567	439	311	218
Mg	37.9	22.7	47.5	24.9	52.0	16.1	65.1	37.2	78.7	40.3
pH	1.87	0.24	2.51	0.57	2.80	0.54	2.63	0.59	2.72	0.40
SO ₄ ^h	9030	4611	6720	4323	3644	1325	3837	1432	3491	908
TOC ^h	21.5	16.8	10.2	4.5	7.92	2.99	9.12	8.68	7.05	3.73
Zn	11.5	23.4	30.0	54.5	24.7	29.4	27.2	25.4	31.5	20.6

	Depth 8.1m n=6		Depth 9.5m n=6		Depth 10.8m n=5		Depth 12.5m n=4	
	\bar{x}	S	\bar{x}	S	\bar{x}	S	\bar{x}	S
Al	144	155	135	53	151	82	176	78
Ca	510	52	544	80	505	47	507	38
EC	4684	1334	4559	884	4680	890	4938	1674
Fe	345	569	352	250	379	474	413	368
Mg	84.4	34.1	95.3	18.1	97.2	26.9	79.8	28.5
pH	3.09	0.99	2.87	0.39	2.68	0.41	2.67	0.53
SO ₄ ^h	2612	1888	3656	807	3889	1354	3858	1242
TOC ^h	9.45	6.07	5.79	3.23	5.92	2.43	7.78	5.14
Zn	29.2	20.5	18.9	8.0	15.8	8.1	13.7	8.8

^anumber of samples
^bmean

^cstandard deviation
^dµmhos/cm

To determine whether a statistical correlation existed between sampling depth and constituent concentrations, Pearson's correlation coefficient was calculated. Log transform data were used where appropriate to calculate the correlation coefficient (refer to "Statistical results of the extract data, p. 29, for details). A sample size of 117 and a 5% level of significance (df = 115, $\alpha = .05$) were used to determine a critical value of 0.25, which was used to assess whether a correlation existed (table 11). These criteria do not determine the strength of the relationship, only whether a relationship exists. Boron, Ba, Be, Zn concentrations and Eh values appeared to have no relationship to sample depth; Ca, Cl, Co, Cu, K, Mg, Mn, Na, and Ni concentrations and pH values seemed to increase slightly with sample depth; constituent concentrations for Al, As, Cd, Cr, Fe, Si, SO₄, TOC, and V and EC values decreased with increasing depth in the piles.

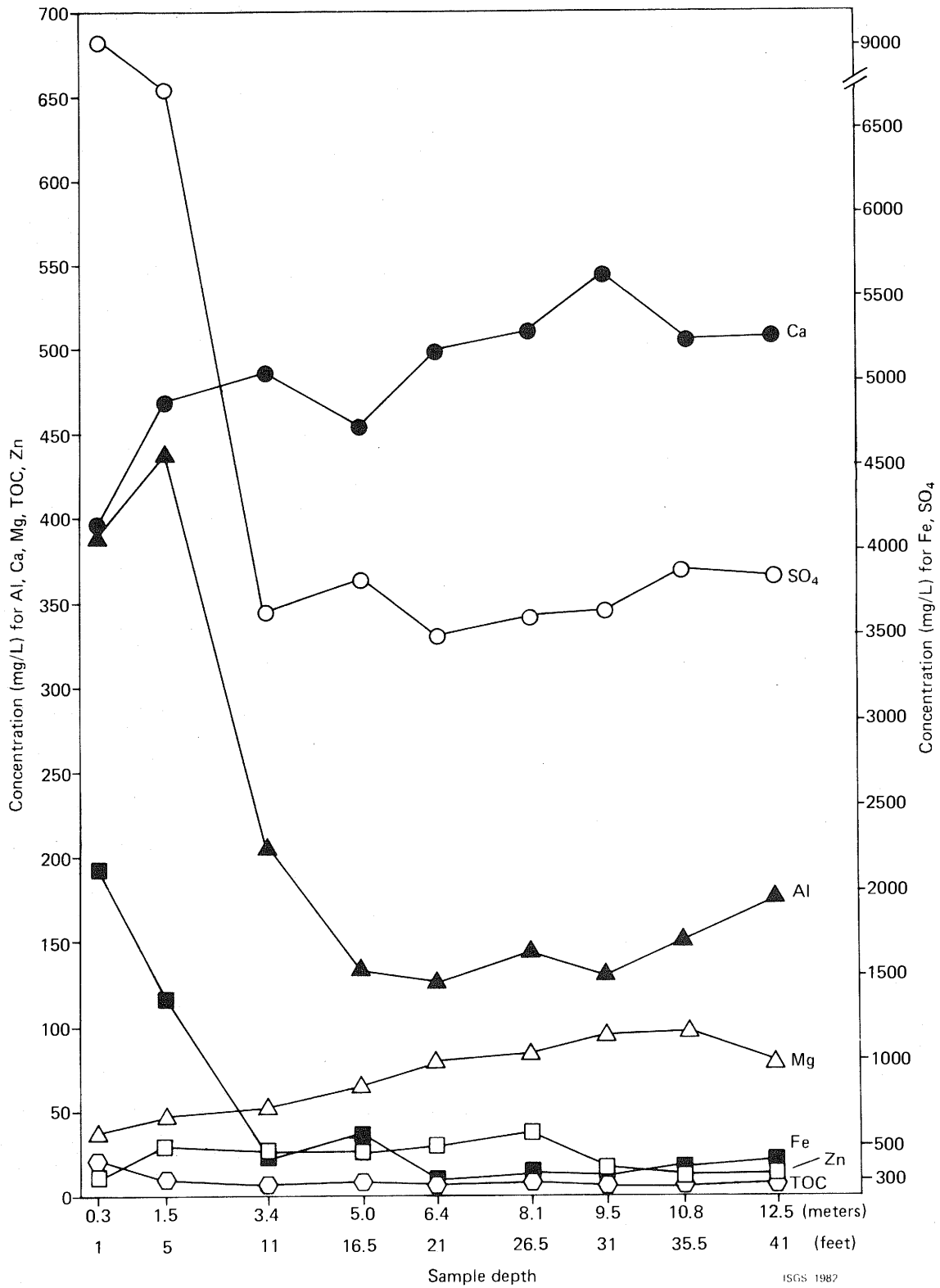


Figure 6. Sample depth and ASTM-A extract concentrations from Little Dog split-spoon samples.

Table 5. Spatial location averages and standard deviations of selected constituent concentrations (mg/L) in the Little Dog ASTM-A extracts.

	Hole B5 n=7 ^a		Hole C2 n=4		Hole E4 n=9		Hole G3 n=12		Hole G6 n=22		Hole H4 n=9	
	\bar{x} ^b	S ^c	\bar{x}	S	\bar{x}	S	\bar{x}	S	\bar{x}	S	\bar{x}	S
Al	366	144	456	257	234	312	118	70	89.4	56.1	220	123
Ca	480	39	416	155	475	36	461	55	508	70	450	65
EC ^d	6493	2235	8881	3590	6306	4322	5165	1565	4148	975	6491	1979
Fe	1385	889	1454	1185	902	1406	549	412	263	220	881	629
Mg	45.0	13.7	29.3	10.5	66.6	28.2	59.3	42.2	45.9	17.4	84.3	47.6
pH	2.48	0.45	2.26	0.89	2.71	0.54	2.53	0.41	2.72	0.38	2.27	0.39
SO ₄	6402	2441	8102	1931	5484	5187	3851	973	2956	662	5425	2133
TOC [†]	10.6	1.5	25.8	27.7	15.1	6.3	7.53	3.97	5.52	2.63	8.03	4.87
Zn	15.3	27.6	38.5	32.0	11.1	10.7	113.7	10.7	16.1	24.1	15.7	17.4

	Hole I5 n=20		Hole J3 n=9		Hole L2 n=8		Hole L6 n=9		Hole M4 n=8	
	\bar{x}	S	\bar{x}	S	\bar{x}	S	\bar{x}	S	\bar{x}	S
Al	156	127	227	87	121	91	656	261	387	20
Ca	505	56	438	129	511	80	422	50	494	58
EC	4898	2036	6500	2946	4502	1674	8532	2531	5668	1298
Fe	415	553	810	700	417	471	2340	1730	526	496
Mg	77.0	27.5	47.6	27.9	84.5	36.4	84.3	21.0	88.9	50.3
pH	2.86	0.79	2.32	0.58	3.20	0.82	2.28	0.11	2.41	0.28
SO ₄	3742	1715	4922	2258	3404	1427	9570	4387	4980	1603
TOC [†]	6.46	4.49	9.28	7.20	20.3	9.3	13.7	5.0	9.60	4.05
Zn	17.6	10.6	11.4	8.0	9.45	4.59	98.0	57.9	65.0	88.0

^anumber of samples
^bmean

^cstandard deviation
^dµmhos/cm

The coefficient of variation (CV) was used to make an initial assessment of variation among extract constituent concentrations. Results indicated that Ca concentration and EC, Eh, and pH values were the least variable, and that Cr and Cu exhibited the greatest variability. Generally, Al, B, Ba, Be, Cl, Co, Mg, Mn, Si, SO₄, and TOC had similar CV values, as did As, Fe, K, Na, Ni, and V. The greatest variability of constituents was found in extracts whose samples were collected between 0.3 and 3.4 m.

Table 5 indicates the variability in constituent concentrations due to sampling location at the Little Dog site. Initial observation indicated that Al, Fe, SO₄, and Zn concentrations were greater in those samples collected around the periphery (B5, C2, L2, L6, M4) rather than the center of the pile. Calcium, Mg, and pH values did not seem affected by sampling location.

Table 6. Summary of constituent concentrations (mg/L) in the Superior Washer ASTM-A extracts.

Constituent	Mean n = 63 ^b	Standard Deviation	CV ^a (%)	Median	Minimum	Maximum
Al	212	99	46.7	195	37.6	485
As	0.61	0.46	75.4	0.55	.05	1.79
B	0.85	0.87	102	0.59	.002	3.88
Ba	0.052	0.031	59.6	0.05	.001	0.15
Be	0.016	0.009	56.3	0.02	.002	0.04
Ca	548	59	10.8	549	273	699
Cd	0.36	0.27	75.0	0.30	.01	1.65
Cl	4.48	2.97	66.3	3.60	1.40	17.5
Co	0.55	0.78	142	0.22	.01	3.49
Cr	0.45	0.40	88.9	0.33	.03	2.10
Cu	1.47	1.47	100	1.12	.01	6.54
EC ^c	6,620	2,082	31.5	6,400	2,240	12,900
Eh ^d	660	26	3.9	656	561	734
Fe	885	601	67.9	773	23.4	2,550
K	2.77	4.05	146	-	1.03	18.6
Mg	13.8	11.5	83.3	10.5	1.84	75.2
Mn	2.87	2.11	73.5	2.61	0.12	10.3
Ni	1.40	1.39	97.3	1.03	0.08	5.92
pH	2.13	0.27	12.7	2.07	1.69	3.39
Si	8.75	3.22	36.8	8.43	3.91	18.4
SO ₄ ⁴⁻	4,998	1,802	36.1	4,755	1,819	10,700
TOC ⁴	10.5	4.3	41.0	9.55	3.69	21.4
V	0.91	0.42	46.2	0.93	.04	1.76
Zn	5.86	10.80	184	1.78	0.30	66.2

^acoefficient of variation = $\frac{\text{standard deviation}}{\text{mean}} \times 100\%$

^bnumber of samples

^cμmhos/cm

^dmillivolts relative to normal hydrogen electrode

To evaluate whether the extracts generated by the ASTM-A procedure were a potential pollution hazard, the mean constituent concentrations in table 3 were compared with drinking and irrigation water standards (U.S. EPA, 1976) as well as the U.S. EPA toxicant extraction procedure criteria for hazardous wastes (U.S. EPA, 1980b). The results indicated that As, Cr, and Cd exceeded primary drinking water standards, but were less than 100 times as great and thus below the EPA extraction procedure criteria for classification as a hazardous waste. Copper, Fe, Mn, SO₄, and Zn concentrations and pH values exceeded the secondary drinking water standards; Al concentrations were greater than irrigation water standards. Those gob piles with leachate pH values less than 2.0 may still be subject to hazardous waste regulation, however, because of corrosivity considerations.

Superior Washer extracts

Constituent concentrations from 63 ASTM-A extracts generated by Superior Washer split-spoon samples are summarized in table 6. The mean extract pH

(2.13) for the Superior Washer extracts was more acidic than that of the Little Dog extracts. The pH exhibited less variability and had a range of 1.69 to 3.39. The ranking of concentrations in the extracts was: $\text{SO}_4 > \text{Fe} > \text{Ca} > \text{Al} > \text{Mg} > \text{TOC} > \text{Si} > \text{Zn} > \text{Cl} > \text{Mn} > \text{K} > \text{Ca} > \text{Ni} > \text{V} > \text{B} > \text{As} > \text{Co} > \text{Cr} > \text{Cd} > \text{Ba} > \text{Be}$; Pb, Mo, Na, Sb, Se, and Sn concentrations were below detection limits. Comparison of the constituent concentrations between the two sites indicated that SO_4 , Fe, Ca, Al, and Mg concentrations were highest, and Ba and Be were the lowest at both sites. In general, the ranking of the remaining constituents was similar. The most soluble constituent, on a weight percent basis, in the Superior Washer extracts was Co, followed by $\text{Ni} > \text{Zn} > \text{Mn} > \text{Cu} > \text{Ca} > \text{As} > \text{SO}_4 > \text{Fe} > \text{V} > \text{Be} > \text{B} > \text{Al} > \text{K} > \text{Ba} > \text{Si}$. Solubilities of the constituents found in Superior Washer and Little Dog extracts followed similar trends.

Means and sample standard deviations of the nine most prevalent constituents in the Superior Washer extracts were calculated. Table 7 summarizes average Al, Ca, Fe, Mg, SO_4 , and Zn concentrations and EC and pH values in which the data were pooled by sample depth without regard to sampling locations. The ranges between the highest and lowest means for the nine parameters in the Superior Washer extracts were compared to the ranges for the same nine constituents in Little Dog extracts (table 4). For all constituents the Superior Washer data showed smaller differences between the highest and lowest means, which indicated less variability among sampling depths.

The means in table 7 are presented graphically in figure 7. Unlike the Little Dog data, Fe and SO_4 concentrations initially increased with sample depth and then decreased until the final mean concentration at 4.0 m was approximately equal to the mean concentration at the 0.3 m depth. The Al concentration for the Little Dog site had the same initial increase in relation to increasing sample depth, but the final mean concentration at 12.5 m was much lower than the initial 0.3 m concentration. The Superior Washer extracts have similar concentrations at 0.3 and 4.0 m. Calcium, Mg, and TOC concentrations remained relatively constant with increasing depth.

Because the Superior Washer site is composed of two different preparation wastes, gob and slurry, extracts generated from both wastes were compared using the t test statistic. This comparison was used to ascertain whether the gob pile could be treated as a homogeneous body with respect to waste type. Results of the t test analyses indicated that only B, Cu, K, and Zn showed significant differences in constituent concentrations of extracts generated by either waste. The F test statistic was used to determine whether the variances in extract constituent concentrations generated from both wastes were equal. Boron, Cl, Cu, K, Mn concentrations as well as EC, Eh, and pH values had unequal variances between gob and slurry; variances for all other constituent concentrations were equal.

Correlation analyses that followed the same criteria established for the Little Dog samples ($df = 61$, $\alpha = .05$, $|r| = 0.25$) were used to determine whether any correlation existed between sampling depth and constituent concentration in the Superior Washer extracts. The findings from the Superior Washer extracts were quite different from the Little Dog extracts. Superior Washer extracts exhibited no correlation between depth and Al, As, Ca, Cr, Fe, SO_4 , and V concentrations, and Eh values. Boron, Ba, Be, Cd, Cl, Co, Cu, Mg, Mn, Ni, and Zn concentrations and pH values showed a slight increase with sample depth; EC, K, Si, and TOC decreased with sample depth. Compared to the Little Dog extracts, fewer constituents exhibited any correla-

Table 7. Sample depth averages and standard deviations of selected constituent concentrations (mg/L) in the Superior Washer ASTM-A extracts.

	Depth 0.3m n=8 ^a		Depth 0.9m n=9		Depth 1.5m n=9		Depth 2.1m n=9	
	\bar{x} ^b	S ^c	\bar{x}	S	\bar{x}	S	\bar{x}	S
Al	166	108	183	73	264	127	220	102
Ca	588	73	544	50	516	43	540	25
EC ^d	5560	1587	7611	2332	7904	2066	7930	2183
Fe	598	538	1149	683	1100	615	1155	664
Mg	9.38	7.77	11.9	4.7	11.8	5.2	12.5	6.2
pH	2.23	0.23	2.00	0.14	1.98	0.13	1.98	0.18
SO ₄	3871	1533	5616	2170	5835	2063	5881	1890
TOC ^h	12.4	4.7	13.2	3.8	11.3	3.1	10.2	5.0
Zn	2.73	3.06	1.89	1.37	1.51	0.92	1.67	1.43

	Depth 2.7m n=8		Depth 3.4m n=8		Depth 4.0m n=5	
	\bar{x}	S	\bar{x}	S	\bar{x}	S
Al	205	84	202	102	180	40
Ca	558	18	540	50	582	44
EC	6450	1444	6125	1648	5284	1258
Fe	861	524	869	599	572	528
Mg	12.1	7.2	17.0	12.3	18.3	18.0
pH	2.11	0.21	2.16	0.23	2.24	0.15
SO ₄	4948	1607	4932	1202	4008	1608
TOC ^h	10.4	4.7	9.06	4.57	9.16	3.28
Zn	5.51	8.38	11.2	14.8	17.7	27.5

^anumber of samples
^bmean

^cstandard deviation
^dµmhos/cm

tions between concentrations and sampling depth and, when a correlation exists, the correlation was weaker for Superior Washer extracts.

The variability of constituent concentrations in the ASTM-A extracts due to sampling location is shown in table 8. No clear trends were apparent from this initial statistical evaluation.

Evaluation of the ASTM-A extracts to determine whether they contained constituent concentrations that might pose environmental hazards revealed findings similar to those of the Little Dog extracts. Arsenic, Cr, and Cd concentrations exceed primary drinking water standards but were below the limits established by the U.S. EPA extraction procedure criteria for determining a hazardous waste. Copper, Fe, Mn, SO₄, and Zn concentrations and pH values exceeded the secondary drinking water standards; Al concentrations were greater than irrigation water standards. Some samples produced extracts with pH values less than 2.0 and might be subject to regulation as a hazardous waste under RCRA due to their corrosivity.

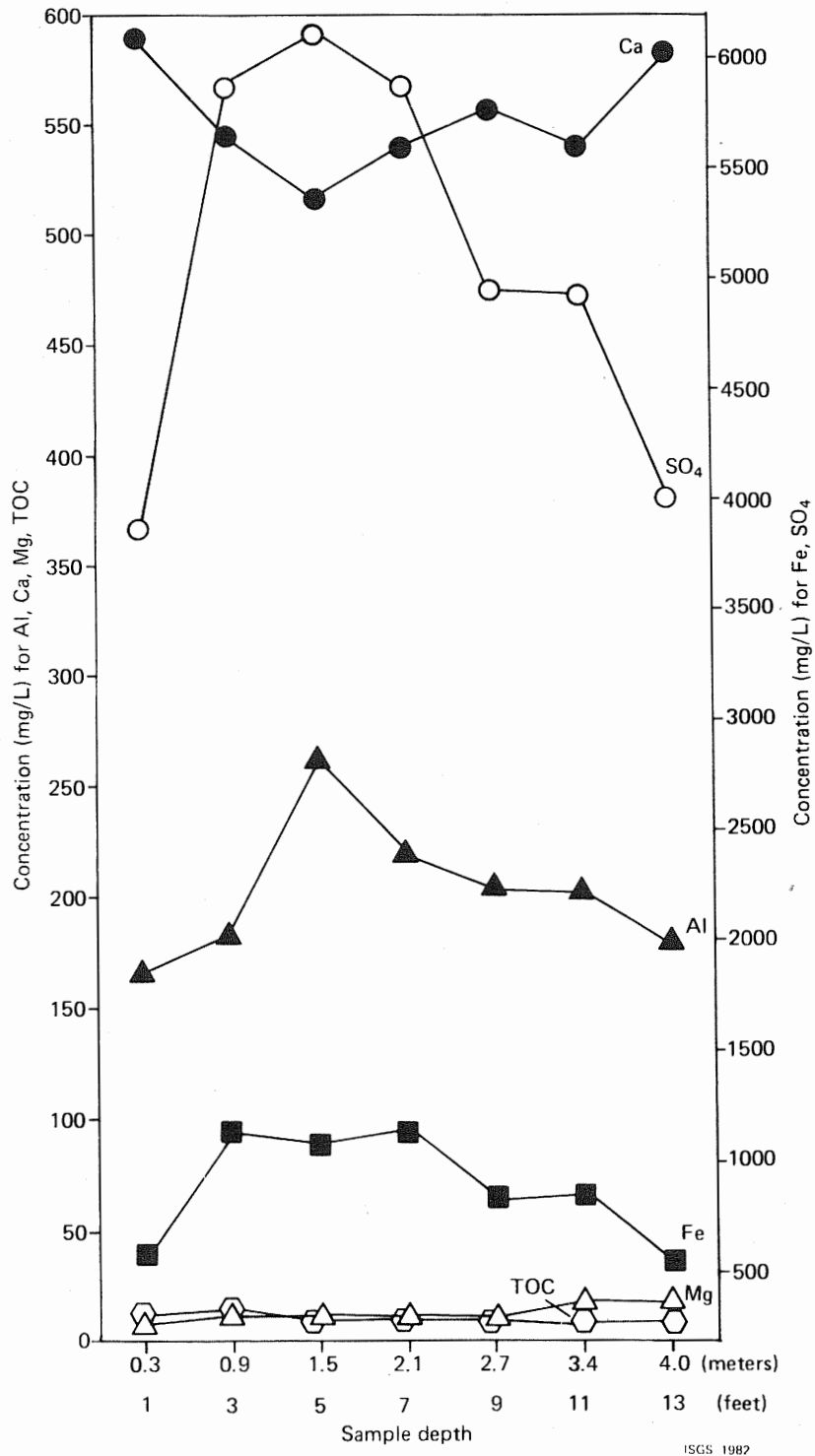


Figure 7. Sample depth and ASTM-A extract concentrations from Superior Washer split- spoon samples.

Table 8. Spatial location averages and standard deviations of selected constituent concentrations (mg/L) in the Superior Washer ASTM-A extracts.

	Hole B4 n=6 ^a		Hole C2 n=8		Hole D6 n=6		Hole F2 n=8		Hole G5 n=8	
	\bar{x} ^b	S ^c	\bar{x}	S	\bar{x}	S	\bar{x}	S	\bar{x}	S
Al	328	109	252	71	207	125	199	122	135	71
Ca	521	58	559	31	568	78	576	33	536	118
EC ^d	9245	2883	6325	1753	6610	2591	6893	1728	5820	2500
Fe	1591	924	889	553	700	615	1049	528	770	646
Mg	17.5	6.5	31.8	20.8	15.9	11.0	9.59	4.66	6.38	3.00
pH	1.90	0.16	2.21	0.22	2.12	0.29	2.11	0.26	2.26	0.53
SO ₄ ⁺	7809	3017	5136	1363	4770	1871	5355	883	4226	1887
TOC	14.7	4.0	7.67	3.78	9.39	2.83	10.0	3.4	11.7	3.4
Zn	1.00	0.70	7.39	5.02	8.50	17.60	19.4	21.6	2.43	3.06

	Hole H7 n=6		Hole I8 n=7		Hole J4 n=10		Hole K6 n=4	
	\bar{x}	S	\bar{x}	S	\bar{x}	S	\bar{x}	S
Al	118	24	225	27	202	32	295	138
Ca	512	49	526	15	560	34	574	50
EC	5743	640	6728	710	6400	2177	6018	1346
Fe	658	226	928	282	776	627	541	426
Mg	6.51	1.73	14.0	5.0	8.98	2.24	14.9	5.4
pH	2.08	0.08	2.08	0.08	2.16	0.22	2.19	0.21
SO ₄ ⁺	4253	677	4930	674	4539	1561	4433	1332
TOC	9.62	4.44	10.9	3.2	11.9	5.9	6.92	2.45
Zn	2.54	3.52	3.97	2.97	2.20	2.11	3.33	1.83

^anumber of samples
^bmean

^cstandard deviation
^dµmhos/cm

STATISTICAL RESULTS OF THE EXTRACT DATA

Logarithmic transformation of data

If univariate statistical tests are used to draw inferences from the data, several basic assumptions have to be met: that observations be independent, have equal variance, and be normally distributed (Scheffe, 1959). Preliminary evaluation of the ASTM-A extract data indicated that the means of many constituents, when grouped by drill hole, were positively correlated with the variance (i.e., greater means were accompanied by greater variances). In many cases, the frequency distributions of the sample extract concentrations were skewed to the right (more smaller concentrations than larger). These results are not uncommon when concentration is the factor being measured (Sokol and Rohlf, 1969). Hence, a common logarithmic transformation was applied to most of the extract results. This resulted in observations with more symmetrical frequency distributions having independent means and similar variances. When data sets had constituent concentrations less than the detection limit of the

instrument measuring the particular constituent, half the detection limit of the instrument (as opposed to zero) was used for the statistical analysis. In all cases Pb, Sb, Se, and Sn concentrations in the extracts were below detection limits and did not undergo any statistical analysis.

Most variants underwent the log transformation. However, Ba, Be, Ca, Eh, Mg concentration, and pH concentration values of the Little Dog samples, and Al, As, Ba, Be, Ca, EC, Eh, and pH values of the Superior Washer samples did not require transformation because they met the assumptions listed above. Means and variances of constituents were compared between study sites: if one set of data required transformation and the other did not, the log transform data were used for both. Throughout the statistical analysis section of this report an "L" before a variate symbol indicates the test statistic was calculated using logarithmically transformed data.

Reproducibility

The reproducibilities of the split-spoon sample preparation and ASTM extraction procedures were determined by randomly selecting three auger cutting samples from each study site and dividing each auger sample into ten subsamples. The subsamples were then subjected to the ASTM-A shake test procedure and the constituent concentrations in the extracts determined. The concentrations for all extract constituents, except pH, underwent log transformation and the mean, standard deviation, and coefficient of variation (CV) were calculated for the extract concentrations from each of the auger samples. Table 9 groups six auger samples that have coefficient of variation values for each extract constituent concentration into four ranges: 1) CV values <5%, 2) CV values >5% but <10%, 3) CV values >10% but <25%, 4) CV values >25%.

For elements such as Ba, Co, K, and V the extreme within-sample variation (as measured by the coefficient of variation) suggests that the ASTM-A extraction procedure and the preparation of the split-spoon samples do not produce homogeneous samples. The variation due to the extraction procedure may be a function of solubility controls, differences in stages of equilibrium and/or the analyses used to determine the concentrations of these constituents. The within-sample variability was greatest for those constituents whose concentrations were near the analytical detection limits. The preparation of the split-spoon samples may be a problem for those constituents in the solids that are in low concentrations.

The contribution of within-sample variance to total variance within a site was estimated by using these replicate results. The extract data generated by the six bulk samples were grouped by site (three samples/site, ten replicates/sample), and a mean variance for each extract constituent concentration was calculated. This mean variance was divided by the variance of the pooled concentration (pooling of constituent concentrations for all extracts for each site regardless of sampling depth or location) and is reported as a percent in table 10. For the most part, the amount of variation contributed by the within-sample variation was less than 5%. Because within-sample variance generally contributed such a small percentage to the overall variances, collection of one sample per depth per hole does not seem unreasonable. Because within-sample variability was small, further investigations were not performed to determine whether within-sample variance was associated with sample preparation, sample splitting, analysis of constituents, nature of the refuse material, the shake test procedure, or a combination of these factors.

Table 9. Number of samples for each constituent having coefficient of variation (CV) values within the ranges listed.

Constituent	CV	CV	CV	CV
	<5%	>5% but <10%	>10% but <25%	>25%
LAl	6			
LAs	2		2	2*
LB	3	2		1
LBa		2	4*	
LBe	4	1	1	
LCa	6			
LCd	4	1	1	
Cl	4	1	1	
LCo			1	5*
LCr	3	2	1	
LCu	1	3		2
EC	6			
Eh	6			
LFe	6			
LK	1	2		3*
LMg	4	1		
LMn	3	1	1	1
LNi	3	1	2	
pH	6			
LSi	6			
LSO ₄	6			
LTOC [†]	6			
LV		2	2	2*
LZn	3	1	1	1

The L before constituent symbol indicates log transform data were used to calculate CV.

*extreme within sample variation

Correlation analysis

Correlation coefficients were calculated to determine whether relationships existed between extract constituent concentrations. As indicated in the overview section of this report, several constituents had positive or negative relationships with respect to sampling depth, such that $|r| \geq 0.25$ was significant at the 5% level for sample sizes of 63 and 117 (Superior Washer and Little Dog samples, respectively). Tables 11 and 12 list those constituents having $|r|$ values ≥ 0.70 for the Little Dog and Superior Washer sites. The tables indicate that correlations exist between EC-SO₄, Fe-SO₄, Fe-V, EC-pH, EC-Fe, EC-V, Fe-pH, pH-V, and Ni-Zn for both study sites. Major differences were found in constituent correlations between the two study sites -- arsenic showed linear relationships with several constituents in the Superior Washer extracts and none in the Little Dog extracts; Cl correlates with Fe, Na, and SO₄ in the Little Dog, but not in the Superior Washer extracts.

The correlation analyses allow for the use of the statistical technique of ratio or regression estimation (Cochran, 1977). The estimation technique approximates the ratio of one constituent to another or predicts the concen-

Table 10. Contribution of within-sample variance to total sample variance.

Constituent	Superior Washer	Little Dog
LAl	0.3 %	0.0 %
LAs	6.0	2.6
LB	0.3	0.0
Ba	5.2	3.4
Be	47.6*	0.9
Ca	13.4*	0.8
LCd	13.0*	0.1
LCl	-	-
LCo	16.5*	2.0
LCr	2.0	0.7
LCu	0.7	0.0
LEC	0.4	0.2
Eh	8.6	1.0
LFe	0.6	0.1
LK	15.0*	10.8*
LMg	0.8	0.1
LMn	3.1	0.1
LNa	-	0.0
LNi	0.4	0.1
pH	0.5	0.1
LSi	2.7	0.7
LSO ₄	0.3	0.4
LTOC ^h	2.3	0.7
LV	2.4	0.3
LZn	4.4	0.1

The L before constituent symbol indicates log transform data were used.

*Constituents in which within sample variance is >10% of total sample variance.

tration of a constituent based on the concentration of another constituent by using their degree of correlation. For example, SO₄ concentrations in the extracts are more difficult and time consuming to determine than Fe, but these constituents are highly correlated ($|r| = 0.85$). Therefore, Fe concentrations for all samples of a large data set, and SO₄ concentrations for a subset of the data set could be made to calculate a correlation coefficient between Fe and SO₄. An overall estimate of the SO₄ concentration for the entire data set could be made from the Fe concentrations and the correlation coefficient. A similar approach could be used if a two-tiered sampling plan was employed in the collection of samples. A correlation coefficient could be determined for constituents from samples collected during the first tier of sampling, and concentrations of those constituents having significant correlation coefficients could be projected for the second tier of sampling. This approach of grouping constituents would reduce the time needed for analysis and thus, costs.

The geochemical interpretations of the correlations for certain extract constituents are beyond the scope of this project and do not directly pertain to sampling. Information regarding the chemistry of acid mine drainage and

Table 11. Correlation of constituents in the Little Dog ASTM-A extracts ($|r| \geq 0.70$).

Constituent	Correlates with	Pearson Correlation Coefficient (r)
LA1	LSO ₄	.81
LA1	LCr ₄	.71
LC1	LNa	.77
LC1	LSO ₄	-.71
LC1	LFe ₄	-.70
LEC	LSO ₄	.94
LEC	LFe ₄	.83
LEC	LV	.82
LEC	pH	-.79
LEh	pH	-.80
LFe	LV	.87
LFe	LSO ₄	.85
LFe	pH ₄	-.81
LNi	LZn	.72
pH	LV	-.82

Table 12. Correlation of constituents in the Superior Washer ASTM-A extracts ($|r| \geq 0.70$).

Constituent	Correlates with	Pearson Correlation Coefficient (r)
Al	Be	.73
As	LV	.83
As	LFe	.82
As	LSO ₄	.81
As	EC ₄	.80
EC	LSO ₄	.91
EC	pH ₄	-.84
EC	LFe	.83
EC	LV	.82
LFe	LSO ₄	.90
LFe	LV ₄	.83
LFe	pH	-.74
LMn	LNi	.73
LNi	LZn	.74
pH	LSO ₄	-.74
pH	LV ₄	-.72
LSO ₄	LV	.89

The L before constituent symbol indicates log transform data were used to calculate correlation coefficient.

interpretations of associated aqueous constituents can be found in Soil Science Society of America (1982); Wewerka, Williams, and Vanderbagh (1978); and Glover (1975).

Comparisons of means for sampling location and depth

Because the sampling plan of this study involved collecting split-spoon samples at various depths from a drill hole, it was important to determine whether spatial relationships existed between samples within the same hole. If spatial relationships did exist, the assumption of sample independence necessary for the analysis of variance tests would be violated. Therefore, the geostatistical technique of calculating a semivariogram to determine spatial relationships was employed. A computer program designed by the United States Geological Survey (David, 1977; Olea, 1977) was used for the semivariogram analysis of several extract constituent concentrations from each site. Results of the semivariogram analyses were inconclusive. A considerably larger number of samples than was obtained for this study would be needed to elicit clear spatial patterns between extract constituent concentrations and sampling depth within a hole. Hence, an assumption of independence between samples was made for the purposes of the statistical analyses discussed below. The assumption of independence between samples is commonly used in sampling plans, such as those used in soil testing (W.M. Walker, Professor of Biometry, Department of Agronomy, University of Illinois, personal communication, 1983).

A two-way analysis of variance (ANOVA) incorporating the Statistical Analysis System (SAS) general linear model (GLM) procedure (SAS, 1979) was used to determine whether the means of constituent concentrations differed with respect to depth or location within a site. Analysis of variance is used to partition variance into components due to the various factors in the experimental design. Differences due to a factor are determined by the magnitude of the ratio of the variance between the levels of a factor to the variance within the levels of a factor, as measured by an F-test (Scheffe, 1959). The SAS GLM procedure compared concentrations of extract constituents generated from samples collected at various depths within the gob pile with concentrations of extract constituents generated from samples collected at various locations of the gob pile. Because the design was unbalanced (i.e., it had different numbers of samples with regard to sampling depth for each hole), the GLM procedure is preferable to the SAS ANOVA procedure. The depth variable, though continuous, was treated discretely and sampling depth intervals were grouped into depth zones to minimize the number of empty cells (no observation for a hole at a certain depth interval) in the model.

Because hole locations were selected at random and the sampling interval and depth as well as the actual depth of the gob pile were fixed, we used a mixed model, two-way ANOVA without interaction. A significant F-test between holes indicated that the level of variability between holes cannot be attributed to sampling error alone; thus, significant differences between holes exist. In the case of a mixed model, Scheffe (1959) stated that the F-test statistic is only an approximation and that the Hotelling's T^2 -test would have to be used to indicate exact differences in extract constituent concentration due to sampling depth and location.

For each extract constituent the Tukey-Kramer comparison of means test was used to determine differences between depth zones, given a significant F-test. Because the hole locations were random, an analysis using the Tukey-

Kramer test was not possible because the assumptions necessary to use this method are different.

The Tukey-Kramer test was performed by using the Tukey option in the means statement of the SAS GLM procedure. The Tukey option uses the harmonic mean of the cell sizes, the mean square for error, and the q statistic to generate confidence intervals for the means of a factor at each level. Unlike the GLM procedure, which simply accepts or rejects a null hypothesis of equal means across levels of a factor (depth or location), the Tukey-Kramer method attempts to show which groups of means are similar, overlapping, and/or dissimilar.

Tables 13 and 14 report the findings of the GLM and Tukey-Kramer analyses for the Little Dog and Superior Washer ASTM-A extracts, respectively. The results in the tables are based on the log transformation of most extract constituent concentrations. The depth zone groupings are indicated in the tables.

In the tables the constituent column (far left column) indicates which extract constituent concentrations as well as whether log concentrations were used in the GLM and Tukey-Kramer tests. The second and third columns (Hole PR>F, Depth PR>F) are the results from the GLM procedure and indicate whether the F statistic was significant. The values reported under this column are the significance probabilities of the F statistic. At a 5% significance level, probability values greater than 0.05 indicate that the means or variance between sample depths or holes are equal. The fourth column contains the results of the Tukey-Kramer test in which constituent concentrations from various sampling depths are compared. The numbers 1 through 12 indicate the depth zones as defined at the bottom of the table (i.e., 1 = 0-0.6 m). The numbers are in groups separated by semicolons; the depths within each group are equal. For example, if log Al concentrations from the Little Dog extracts are used (table 13), the GLM procedure determines the significant probabilities for hole and depth to be 0.0001. This suggests differences in extract Al concentrations due to sampling depth and location. The Tukey-Kramer test divides the depth zones into three overlapping groups. In the depth groups for Al, however, the depth zones 3=1=2 tend to group separately from depth zones 10=9=7. This suggests that the extract Al concentrations from the top 0-1.8 m of the pile are different from the 3.7-9.5 m (middle) regions of the pile. For the Little Dog site (table 13), the GLM procedure rejected the hypothesis that there is no variability between holes for all extract constituents. Changes in extract concentration due to sample depth were found to be significantly different for all extract constituents except Cd and K.

Results of the analysis of variance for the Superior Washer extract data (table 14) showed that As, Ca, Cd, Cl, Eh, Fe, pH, and V concentrations were not different for sampling location (hole). The mean concentrations of five of the 24 constituents (As, Ca, Cd, Eh, Mn) were not statistically different in relation to depth zones. Unlike the Little Dog extracts, the Superior Washer extracts tend to be less affected by sampling location.

The histories of the two gob piles may partly explain some of the differences observed in the statistical analyses. The Superior Washer site received material from several mines, which initially suggested a greater variability of material than the Little Dog site (which received material from only one mine). However, upon closer inspection of the Superior Washer site, it appears that the gob was spread over a thin layer of slurry. Spreading the

Table 13. Comparison of means and variances showing effects of sampling location versus sampling depth for constituents in the Little Dog ASTM-A extracts.

Constituent	Hole ^a PR>F	Depth ^a PR>F	Comparison of means for sampling depth ^b
LAl	.0001	.0001	3=1=2=4=12=5=6=11; 4=12=5=6=11=8; 12=5=6=11=8=10=9=7
LAs	.03	.008	1=2=3=11=5=12=4=6=7=8; 3=11=5=12=4=6=7=8=9=10
LB	.0001	.0004	10=5=6=7=8=9=11=4=1=12=3; 11=4=1=12=3=2
Ba	.0001	.002	1=11=2=10=12=3=8=6=9=7=4=5
Be	.0001	.07	3=5=4=11=6=12=2=8=1=9=10=7
Ca	.02	.0001	10=9=11=12=4=6=7=8=5=3; 4=6=7=8=5=3=1; 6=7=8=5=3=1=2
LCd	.0001	.65	
LCI	.0001	.0001	9=8=10=12=11=7=5=6; 12=11=7=5=6=4; 4=3=2; 3=2=1
LCo	.0004	.0001	10=8=11=9=5=3=6=7=4=12; 11=9=5=3=6=7=4=12=2; 12=2=1
LCr	.0001	.01	1=2=4=5=3=6=8; 2=4=5=3=6=8=7=11=9=10=12; 1=4=9=8=12=6=7=10=3=2=1
LEC	.0001	.0001	4=5=12=8=11=9=7=6=10
Eh	.0001	.005	1=2=9=11=8=12=7=6; 2=9=11=8=12=7=6=3=5=4
LFe	.0001	.0001	2=1=3=4=5; 3=4=5=12=6=8=7=11; 4=5=12=6=8=7=11=9; 5=12=6=8=7=11=9=10
LK	.03	.78	
Mg	.0001	.0001	9=10=11=7=8=12=5=4=6; 11=7=8=12=5=4=6=3; 7=8=12=5=4=6=3=1; 4=6=3=1=2
LMn	.002	.0001	9=8=7=10=12=6=5=11=4; 8=7=10=12=6=5=11=4=3; 11=4=3=2; 4=3=2=1
LNa	.0001	.0001	10=8=11=9=7=12; 11=9=7=12=6; 7=12=5=4=6=3; 6=5=4; 4=1=3=2
LNi	.0001	.0001	8=9=10=11=7=5=6=12=3=4; 5=6=12=3=4=2; 2=1;
pH	.0005	.0001	10=9=6=5=7=8=11=4=12=3; 7=8=11=4=12=3=2; 3=2=1
LSi	.0001	.05	1=2=6=3=4=8=12=7=11=9; 2=6=3=4=8=12=7=11=9=10=5
LSO ₄	.0001	.0001	1=2=3; 2=3=4=5; 4=5=11=12=6=8=9=10=7
TOC ⁴	.0001	.0001	1=2=5=4=3; 2=5=4=3=9=6=12=7; 3=9=6=12=7=10=8; 9=6=12=7=10=8=11
LV	.0001	.0001	1=2=3=4=5; 2=3=4=5=12=11; 3=4=5=12=11=6=7=8; 10=9
LZn	.0001	.0001	8=9=5=4=6=7=10=11=3=12; 9=5=4=6=7=10=11=3=12=2; 12=2=1

The L before constituent symbol indicates log transform data were used to calculate test statistic.

^aIf PR>F is greater than .05, all means are equal.

^bDepth zones: 1=0-.60m; 2=.61-1.20m; 3=1.21-1.80m; 4=1.81-2.40m; 5=2.41-3.00m;
6=3.01-3.70m; 7=3.71-4.90m; 8=4.91-6.40m; 9=6.41-7.90m;
10=7.91-9.50m; 11=9.51-11.0m; 12=11.01-13.1m

Table 14. Comparison of means and variances showing effects of sampling location versus sampling depth for constituents in the Superior Washer ASTM-A extracts.

Constituent	Hole ^a PR>F	Depth ^a PR>F	Comparison of means for sampling depth ^b
Al	.0002	.06	8=3=4=7=5=6=2; 3=4=7=5=6=2=1
As	.13	.24	
LB	.01	.0001	7=6=8=5=4=3; 8=5=4=3=2; 5=4=3=2=1
Ba	.02	.006	8; 3=5=6=4=7=2=1
Be	.001	.02	8=3=6=7=5=4=1=2
Ca	.37	.27	
LCd	.55	.18	
LCI	.24	.0003	8=7=5=6; 5=6=4=3=1=2
LCo	.0001	.03	8=6=5=3;4 7=2; 6=5=3=4=7=2=1
LCr	.01	.02	3=5=4=2=6=8=7; 4=2=6=8=7=1
LCu	.02	.0002	5=6=8=7=3=4=2; 4=2=1
EC	.03	.001	4=3=2=5=6=1=7; 5=6=1=7=8
Eh	.52	.30	
LFe	.22	.03	2=3=4=5=6=7=1; 3=4=5=6=7=1=8
LK	.002	.0003	3=4=2=5=6=1; 2=5=6=1=7=8
LMg	.0001	.002	7=6=4;8 2=3=5; 4=8=2=3=5=1
LMn	.02	.29	
LNi	.0001	.004	8=6=7=5=4=3=2; 6=7=5=4=3=2; 6=7=5=4=3=2=1
pH	.33	.003	8=7=1=6=5; 7=1=6=5=2=3=4
LSi	.001	.0001	1=2=3; 3=4=5=6; 4=5=6=7=8
LSO	.02	.03	4=3=2=6=5=7=8=1
LTOC [†]	.001	.001	2=1=3=5=4=7=6; 5=4=7=6=8
V	.23	.04	3=4=5=2=6=7=1=8
LZn	.0004	.0002	8=7=6=5; 6=5=2=1=4=3

The L before constituent symbol indicates log transform data were used to calculate test statistic.

^aIf PR>F is greater than .05, all means are equal.

^bDepth zones: 1=0-.60m; 2=.61-1.20m; 3=1.21-1.80m; 4=1.81-2.40m; 5=2.41-3.00m; 6=3.01-3.70m; 7=3.71-4.90m; 8=4.91-6.40m; 9=6.41-7.90m; 10=7.91-9.50m; 11=9.51-11.0m; 12=11.01-13.1m

gob caused mixing to occur, which might have resulted in a more homogeneous blend of waste than that found at the Little Dog site. The plateau shape (which would allow more uniform percolation of water) and the relatively shallow depth of the Washer site could also cause the changes in the gob that are caused by weathering, erosion, etc. to be more uniform throughout the site.

The Tukey-Kramer results did not completely separate the extract data by any depth zone grouping for either study site. Because of the great amount of overlap, patterns due to depth were not clear-cut, although certain trends were observed. The results of the Tukey-Kramer procedure suggested a tendency for the Superior Washer extracts to group into "top", "middle", and "bottom" regions; the Little Dog extracts group either into "top", "middle", and "bottom" or "top and bottom" versus "middle" regions.

Clarifying the trends in constituent concentration due to sampling depth would likely require increasing the number of samples taken from a site. To explore some of the initial trends observed, we pooled the extract data into fewer, larger depth zones. Pooling simulates increased numbers of samples by increasing the numbers of samples within a depth zone, and decreasing the number of zones. The extract data from the Superior Washer site were grouped into three depth zones: 1) 0-1.5 m, 2) 1.6-3.4 m, 3) >3.4 m. The Little Dog extract data were grouped into five depth zones: 1) 0-1.5 m, 2) 1.6-3.4 m, 3) 3.5-5.8 m, 4) 5.9-9.5 m, 5) >9.5 m. These depth zones were chosen because they represented the inflection points in the concentrations illustrated in figures 6 and 7. The SAS GLM procedure and the Tukey-Kramer comparison of means were again applied to the extract data and the depth zones indicated above were used.

The results of the analysis of variance of the Little Dog extract data that incorporated fewer depth zones indicated that all constituents were significantly related to sampling location (hole). All but four analytes (Be, Cd, K, Si) were significantly related to sampling depth (table 15). For those 20 constituents that were significantly different, a clearer pattern between constituent concentration and sample depth emerged. Concentrations in the first depth zone (0-1.5 m) grouped separately from the other four zones 12 out of 20 times, and one out of 20 times with the 1.6-3.4 m depth zone. The ordering of means, according to the depth zones, occurred 14 out of 20 times as: 1=2=5, 1=5=2 or 1=5=3/4.

When compared to the previous analysis that used one observation per cell, fewer differences in constituent concentration due to depth and hole location were evident. Fourteen and 12 constituents out of the possible 24 showed differences due to sampling location (holes) and depth, respectively, in the Superior Washer extracts. The previous results indicated 16 and 19 constituents were significantly different due to sampling location and depth, respectively.

The Tukey-Kramer comparison clearly distinguishes a grouping pattern in 12 of the 14 Superior Washer extract constituents that were significantly different due to depth (table 16). For five constituents (Cl, EC, K, pH, Zn) the top and middle regions (0-3.4 m) grouped separately from the bottom region (>3.4 m), and four constituents (B, Cu, Ni, Si) grouped at the top (0-1.5 m), separately from the middle and bottom regions (2.1 m->3.4 m).

Results of decreasing the number of depth zones and increasing the sample sizes within each depth zone are: 1) increasing sample size increases the resolution of patterns between constituent concentrations in the extracts and sampling depth, 2) increasing sample size decreases the number of constituents showing significant differences due to sampling location and depth, 3) of those constituents in the Superior Washer extracts exhibiting differences due to sampling depth, the concentrations of the constituents whose samples were collected from the top and middle region (0-3.4 m) were different from those of the bottom region (>3.4 m), 4) concentration of the Little Dog extracts sampled collected from the top (0-1.5 m) were different than those sampled from the middle (4.0-9.5 m) and bottom (>9.5 m) regions.

In summary, results of the analysis of variance showed differences in extract constituent concentrations due to sampling location and depth. There is significant variability between holes at each site. Grouping the data so that there were fewer depth zones but larger numbers of samples in each zone

Table 15. Comparison of means and variances with decreased number of depth zones for constituents in the Little Dog ASTM-A extracts.

Constituent	Hole ^a PR>F	Depth ^a PR>F	Comparison of means for sampling depth ^b
LAl	.0001	.0001	1; 2=5; 4=3
LAs	.03	.0013	1=5=2; 5=2=3=4
LB	.0001	.0001	4=2=3=5; 5=1
Ba	.0001	.0003	1=5=4; 5=4=3=2
Be	.0001	.07	
Ca	.0096	.0001	4=5=2=3; 1
LCd	.0001	.33	
LCl	.0001	.0001	4=5=3; 3=2; 1
LCo	.0018	.0001	4=3=2=5; 5=1
LCr	.0001	.0020	1=2; 2=3; 3=4=5
LCu	.0055	.0023	2=5=3=4; 3=4=1
LEC	.0001	.0001	1; 2=5=3=4
Eh	.0001	.081	
LFer	.0001	.0001	1; 2=5=3; 5=3=4
LK	.02	.42	
Mg	.0001	.0001	4=5=3; 5=3=2; 1
LMn	.0013	.0001	4=3=5=2; 1
LNa	.0001	.0001	4=3=5; 2; 1
LNi	.0001	.0001	4=3=5=2; 1
pH	.0007	.0001	4=2=3=5; 1
LSi	.0001	.10	
LSO	.0001	.0001	1; 2=5=4; 5=4=3
TOC ⁴	.0001	.0008	1=2; 4=5=3
LV	.0001	.0001	1; 2=5=3=4
LZn	.0001	.0001	4=2=3=5; 5=1

The L before constituent symbol indicates log transform data were used to calculate test statistic.

^aIf PR>F is greater than .05, all means are equal.

^bDepth zones: 1 = 0 to 1.5 m; 2 = 1.6 to 3.4 m; 3 = 3.5 to 5.8 m;
4 = 5.9 to 9.5 m; 5 = >9.5 m.

revealed that some patterns develop between sample depth and concentration. By developing a sampling plan where each sampling depth is more thoroughly sampled, a clearer pattern between constituent concentrations, sample depth, and location may become apparent.

Comparison of means and variation between sites

Two methods of statistical analysis were used to determine whether the mean concentrations in the Little Dog extracts were equal to those in the Superior Washer extracts. The composite method employs the Student's *t*-test, and pools the data, i.e., treats the data as if from a sampling of the population regardless of spatial location in the pile. The other method, an analysis of variance approach (ANOVA), considers variations due to sampling depth and location within each site before comparing the sites.

Table 16. Comparison of means and variances with decreased number of depth zones for constituents in the Superior Washer ASTM-A extracts.

Constituent	Hole ^a	Depth ^a	Comparison of means for sampling depth ^b
	PR>F	PR>F	
Al	.0006	.26	
As	.15	.11	
LB	.02	.0001	3=2; 1
Ba	.02	.38	
Be	.0033	.04	3=2=1
Ca	.44	.99	
LCd	.54	.44	
LCI	.25	.0001	3; 2=1
LCo	.0001	.04	3=2=1
LCr	.02	.44	
LCu	.10	.0012	2=3; 1
EC	.08	.01	1=2; 3
Eh	.67	.30	
LFe	.28	.08	
LK	.0090	.01	1=2; 3
LMg	.0001	.0021	3=2; 2=1
LMn	.02	.12	
LNi	.0001	.0019	3=2; 1
pH	.50	.0028	3; 2=1
LSi	.0015	.0001	1; 2=5
LSO	.04	.08	
LTOC ^h	.0031	.0002	1=2; 2=3
V	.31	.19	
LZn	.0016	.0001	3; 2=1

The L before constituent symbol indicates log transform data were used to calculate test statistic.

^aIf PR>F is greater than .05, all means are equal.

^bDepth zones: 1 = 0 to 1.5 m; 2 = 1.6 to 3.4 m; 3 = >3.5 m.

The pooled method is the simplest approach and uses the "usual" sample mean (\bar{x}) and variance (s^2) calculations:

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (1)$$

$$s^2 = \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1} \quad (2)$$

where n = sample size
 x_i = observations.

The \underline{t} - test statistic assumes equal variances for the two populations, with degrees of freedom equal to the sum of the sample sizes minus two (Sokol and Rohlf, 1969). The \underline{t} - test statistic was calculated by:

$$\underline{t} = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\left[\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \right] \left[\frac{n_1 + n_2}{n_1 n_2} \right]}} \quad (3)$$

where \bar{x}_1 = mean of population 1

\bar{x}_2 = mean of population 2

s_1^2 = variance of population 1

s_2^2 = variance of population 2

n_1 = sample size of population 1

n_2 = sample size of population 2.

The analysis of variance used the SAS GLM procedure (SAS, 1979), which nests hole location and depth within site (i.e., partitions variances due to location or depth within-site) and compares the effect of hole location and depth without using an interaction term.

The results generated by the hypothesis tests, which determined whether the mean concentration of constituents between sites were significantly different, are given in table 17. The \underline{t} - test and ANOVA results yielded similar conclusions. In both cases Al, B, Si, and SO₄ concentrations in the ASTM extracts were not significantly different between sites. In addition, the pooled \underline{t} - test method found Cd and Cu concentrations similar between sites; the ANOVA method found EC, Fe, and TOC concentrations similar. Both methods indicated that all other constituents in the extracts were different between sites at the 5% significance level. Because 15 of the 24 constituent concentrations in the extracts were different between sites, the two sites are probably different from each other.

Comparison of the two sites indicated marked differences. Most concentrations of extract constituents were significantly different, and levels of variation differed for each constituent. Although many of these differences in variation were not statistically significant, they still affected determinations of sample numbers necessary to achieve a certain degree of representativeness for a particular constituent. Hence, a universal sampling protocol for gob piles does not seem likely; each pile must be treated individually and a sampling scheme developed on the basis of the variability of each pile. However, these findings are based on only two gob piles. When more piles have been studied, similarities among piles may be found.

Table 17. Comparison of means for the Superior Washer and Little Dog sites.

Constituent	Composite	ANOVA
LA1	NS	NS
LAs	***	***
LB	NS	NS
Ba	***	***
Be	***	***
Ca	***	***
LCd	NS	*
LCl	***	***
LCo	***	***
LCr	***	***
LCu	NS	**
LEC	**	NS
Eh	***	***
LFe	**	NS
LK	**	*
LMg	***	***
LMn	***	***
LNi	***	***
pH	***	***
LSi	NS	NS
LSO ⁴	NS	NS
LTOC ⁴	*	NS
LV	***	***
LZn	***	***

The L before constituent symbol indicates log transform data were used to calculate t statistics.

- NS not significantly different.
- *** significantly different $\alpha = .001$ (99.9%).
- ** significantly different $\alpha = .01$ (99.0%).
- * significantly different $\alpha = .05$ (95.0%).

DESIGN OF A SAMPLING PROTOCOL

A variety of designs for developing sampling schemes are available (Cochran, 1977; Krumbein and Graybill, 1965; Gy, 1982). Of primary concern in designing a sampling scheme are: 1) cost, 2) developing objectives to be investigated, 3) defining the population of interest, 4) selecting variables to be measured so the objectives can be fulfilled, 5) identifying sources of variability that need to be taken into account when sampling, 6) determining the number of samples required so that the objectives can be determined within a defined error, and 7) developing appropriate statistical models to analyze the data. For the remaining portion of this report, "sample size" will be used interchangeably with "the number of samples" (e.g., number of split-spoon or auger cuttings required to achieve a required variance, level of accuracy, or cost).

In developing a sampling scheme to collect representative gob samples for leaching studies, several factors must be considered. The initial assumption that the gob pile in question is heterogeneous requires that samples be collected at various depths and locations throughout the pile. In this study this assumption was verified by the general linear model (GLM) and Tukey-Kramer results; significant differences in extract concentrations were found for samples collected at various depths and locations in the gob pile. Therefore, a stratified sampling plan where sampling locations are equidistant and equally represent the gob pile should be employed. The costs of gaining access to the pile, setting up a drill rig and collecting, preparing, and analyzing samples must also be considered.

Prior knowledge of the variability of the gob pile, such as variances between sampling locations (holes) or depths and variances due to analytical techniques, can be used to determine the number and kinds of samples required to achieve a defined level of accuracy in the results. Several methods of determining sample sizes necessary to minimize costs and variability or to increase accuracy are outlined below.

Determination of sample sizes using a t distribution

By a Central Limit Theorem of probability theory, given the sample mean (\bar{x}) and variance (s^2), it is possible to construct confidence intervals for the true mean of the population samples:

$$\bar{x} \pm \frac{s}{\sqrt{n}} t_{(\alpha/2, n-1)}$$

The confidence interval can be used to estimate the number of samples (n) necessary to achieve a sample mean within a given proportion (r) of the population mean (precision) at a level of confidence ($1 - \alpha$). Thus, if:

$$\bar{x} \pm \frac{s}{\sqrt{n}} t_{(\alpha/2, n-1)} = \bar{x} \pm r \bar{x},$$

solving for n (sample size):

$$n = \left[\frac{t_{(\alpha/2, n-1)} s}{r \bar{x}} \right]^2 \quad (4)$$

However, this formula must be solved by iteration because the degrees of freedom ($n-1$) for the t value change with n . By relaxing the conditions somewhat, a fixed value of t could be used. Choosing a value of $t = 2$ allows n to be solved for a confidence interval of ± 2 standard errors. Because only an approximate value of n is possible, this simplification is most reasonable as a first approximation. Note also that for large numbers of samples (n), $t_{(\alpha=.05, 60)} = 2$ and at $n = 120$, t is for all practical purposes the same as the normal distribution with $t_{.05} = Z_{.05} = 1.96$. The sample sizes reported in tables 18 and 19 have been calculated to estimate within 5%, 10%, and 25%, at a 95% confidence interval of the true water soluble constituent concentration in the refuse piles (such that $r = .05, .1, .25$ in formula 4). These sample sizes are specific to the sampling methods and the sites of this study: 1) split-spoon sampling at 0.6 m intervals, 2) analysis of samples using the ASTM-A shake test procedure as opposed to solid analysis and, 3) coal refuse material generated by the mining of Herrin (No. 6) Coal. However, the sample

sizes listed may serve as a guide for a first sampling in a tiered sampling scheme at other sites.

A pooling method using a t distribution is statistically the simplest of the methods discussed. It pools the extract data for each site without regard to sample depth or location. On the basis of 11 and seven samples per hole for the Little Dog and Superior Washer sites, respectively, these results indicate the number of individual samples to be collected. For both the Superior Washer and Little Dog sites, the analytes Al, Ca, Cl, EC, Eh, Fe, Mg, pH, Si, SO_4 , and TOC required sample sizes between one and 65 samples at the 10% error level. Sample sizes at the 10% level for Co, Cu, K, Ni, and V were large, which suggests that the extract concentrations would be difficult to estimate with a high degree of accuracy. Few constituents have "practical" sample sizes at the 5% error level.

As demonstrated, both sample depth and location have been shown to affect constituent concentrations. To focus on the variability between holes, the mean concentration of a completely sampled hole may be used as an estimate of the population concentration. The investigator could continuously sample a hole, and analyze one composite sample from each hole. This would reduce the number of samples to be analyzed and allow more holes to be sampled. Also, the investigator could analyze several subsamples of the composite sample and introduce an error term into the statistical evaluation of the data to account for analytical variability. This may be less expensive than taking a large number of split-spoon samples.

Although the sampling methodology of this project did not involve compositing samples per hole, the data were grouped to simulate compositing. However, due to solubility controls and interactions between soluble constituents (i.e., adsorption, precipitation), the concentration of extract constituents -- determined by averaging the observations (individual split-spoon sample extracts) for each hole -- may not represent the concentrations of extract constituents as accurately as if the solid split-spoon samples for each hole were combined and then subjected to the ASTM shake test. Averaging concentrations of the extracts from the available data from each hole is a reasonable approximation of a "composite" extract. For the Superior Washer data, a simple average of the observations for each hole was used as a "composite" estimate because these holes were continuously sampled. Because the entire hole was sampled, this composite mean would have no variance and would simulate a true, single composite observation.

Unlike the Superior Washer site, most holes of the Little Dog site were not continuously sampled. Because the number of possible samples collected at 0.6 m intervals for each hole is a function of hole depth (and hence a finite number), a finite population correction factor (fpc) was introduced for this discontinuous sampling without replacement. When all possible samples are collected, the composite mean of a hole has no variance. If a hole is only partially sampled, the variance of the mean of the hole is calculated by:

$$S_c^2 = \left(\frac{N_i - n_i}{N_i - 1} \right) \frac{s_i^2}{n_i} \quad (5)$$

where N_i = all possible samples (depth of hole)
 n_i = number of samples collected
 s_i = variance of the observations in the hole.

In those holes where incomplete sampling occurred, the variance of the mean was usually less than 15% of the variance between different hole means and ranged from 3% to 50%. On the basis of these findings, the means for holes at the Little Dog site were treated as if completely sampled, and the variance within a hole equal to zero.

Because the variability within a hole is zero, the variability between different hole means was calculated by:

$$s_H^2 = \frac{\sum(\bar{x} - \bar{x}_i)^2}{(n_H - 1)} \quad (6)$$

where \bar{x} = the unweighted mean of the hole means
 \bar{x}_i = mean of hole i
 n_H = number of holes.

The number of samples required for each error level (5%, 10%, and 25%) can be calculated by substituting the variance between holes (s_H^2) where each hole is considered as a single composite sample for the variance (s^2) in formula 4. The results (tables 18 and 19) represent the number of holes where one composite sample per hole was collected.

Histograms are presented to summarize the results of sample sizes for the various extract constituents. The number of samples shown in these figures was generated by using the composite grouping of the extract data and estimating the sample mean within $\pm 10\%$ of the population mean for a 95% confidence interval. The visual representation of sample sizes for each extract constituent in the histograms (figs. 8 and 9) allows constituents to be easily grouped according to sample sizes. Generally, constituents for both sites could be placed into three groups by sample sizes: 1-50, 51-150 and >150. Aluminum, Ca, Cl, EC, Eh, Fe, Mg, pH, Si, SO_4 , and TOC required that less than 50 samples be collected for the sample mean to be within 10% of the population mean; at the other extreme, B, Co, Cu, K, and V required more than 150 samples, which made estimates for these constituents difficult. Note that these latter constituents are the same elements that showed large amounts of within-sample variance discussed earlier in the report. Chromium was the only constituent for both sites that required between 51 and 150 samples to estimate the mean concentration of the pile within 10%.

Differences in sample sizes between the two sites were evident. A two-fold or greater increase in the number of samples for the Little Dog Al, Ba, Be, Cd, Cl, and TOC extract constituents was necessary for the sample mean to be within 10% of the population mean. The Superior Washer site required sample sizes for As, Mg, Mn, Ni, and Zn to be twice as great as the corresponding Little Dog sample sizes. These differences in sample number requirements between sites reflect the amounts of variation present for each constituent. The more variation an extract constituent exhibits within a refuse pile (or within a sample), the greater the sample number required to have precision equal to those constituents exhibiting less variation.

Table 18. Number of Little Dog samples to attain a sample mean within \pm 5%, 10%, or 25% of the population mean.

Constituent	Pooled			Composite		
	5%	10%	25%	5%	10%	25%
LAl	64	16	3	30	8	2
LAs	562	141	23	23	133	6
LB	3,197	800	128	1,175	294	47
Ba	1,267	317	51	687	172	28
Be	614	154	25	300	75	12
Ca	38	10	2	9	3	1
LCd	1,033	259	42	758	190	30
LCI	259	65	11	146	37	6
LCo	2,614	654	105	615	154	25
LCr	502	126	21	351	88	14
LCu	5,883	1,471	236	1,465	367	59
LEC	3	1	1	2	1	1
Eh	9	3	1	5	2	1
LFe	72	18	3	23	6	1
LK	3,591	898	144	1,466	367	59
LMg	33	9	1	13	4	1
LMn	316	79	13	103	26	5
LNi	1,069	268	43	478	120	20
pH	76	19	3	21	6	1
LSi	55	14	3	22	6	1
LSO ₄	6	2	1	3	1	1
LTOC _h	148	37	6	64	16	3
LV	1,816	454	73	1,226	307	50
LZn	345	87	14	150	38	6
mean (n=24)	982	246	40	385	97	16

The L before constituent symbol indicates log transform data were used to calculate sample sizes.

Although many of the sample sizes are extreme, and collection of such a large number of samples would be impractical, the sample sizes reflect the variability of the water soluble constituents in the coal refuse piles. Depending on how representative the sampling plan needs to be, an investigator can alter the level of significance or percent error to accommodate his finances, analytical capabilities, and time schedule. The sample size needed will be reflected by the hypothesis in question. If one is interested only in generating a representative estimate of the pile, then the composite method (a composite sample of each hole with several replicates of each sample) probably provides the best estimate. The pooled method, with uniform sampling over depth and location, might provide trend information as well as an estimate of the pile concentration.

Table 19. Number of Superior Washer samples to attain a sample mean within ± 5%, 10%, or 25% of the population mean.

Constituent	Pooled			Composite		
	5%	10%	25%	5%	10%	25%
LAl	14	4	1	7	2	1
LAs	2,545	637	102	427	107	18
LB	5,272	1,319	211	1,331	333	54
Ba	549	138	22	161	41	7
Be	481	121	20	154	39	7
Ca	19	5	1	4	1	1
LCd	718	180	29	101	26	5
LCI	228	57	10	40	10	2
LCo	1579	395	64	938	235	38
LCr	1086	272	44	365	92	15
LCu	23,509	5,878	941	4,871	1,218	195
LEC	3	1	1	1	1	1
Eh	3	1	1	1	1	1
LFe	31	8	2	6	2	1
LK	35,684	8,921	1,428	8,655	2,164	347
LMg	110	28	5	64	16	3
LMn	2,646	662	106	822	206	33
LNi	53,891	13,473	2,156	26,862	6,716	1,075
pH	25	7	1	4	1	1
LSi	47	12	2	13	4	1
LSO	3	1	1	1	1	1
LTOC	57	15	3	18	5	1
LV	12,407	3,102	497	2,253	564	91
LZn	3,005	752	121	1,053	264	43
mean (n=24)	5,997	1,500	240	2,006	502	81

The L before constituent symbol indicates log transform data were used to calculate sample sizes.

Determination of sample sizes using cost and variance functions

A more sophisticated method for determining a sampling scheme using the data generated by this study involves an optimal allocation of resources approach. From the GLM results, the variation in each site can be partitioned as the variance between holes (V_H), the variance between depth zones (V_D) and a sampling error variance (V_E). Assuming interaction to be zero and the mean square for error (MSE) to be an estimate of V_E , V_H and V_D can be estimated from their respective mean squares (MSH and MSD, respectively) adjusted for

$$V_H = \frac{MSH - MSE}{\text{degrees freedom depth} + 1}$$

$$V_D = \frac{MSD - MSE}{\text{degrees freedom hole} + 1}, \text{ (Sokol and Rohlf, 1969; Scheffe, 1959).}$$

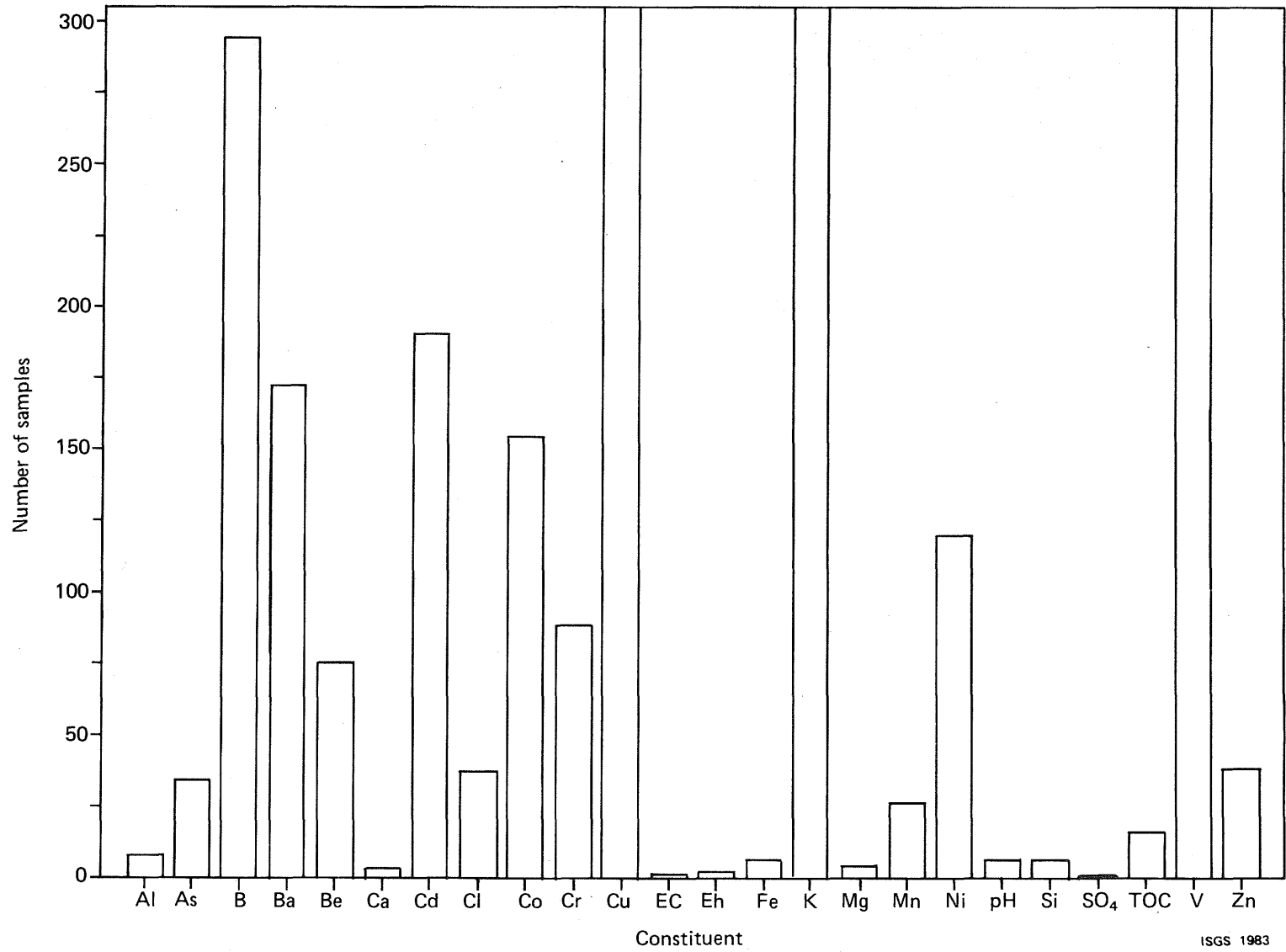
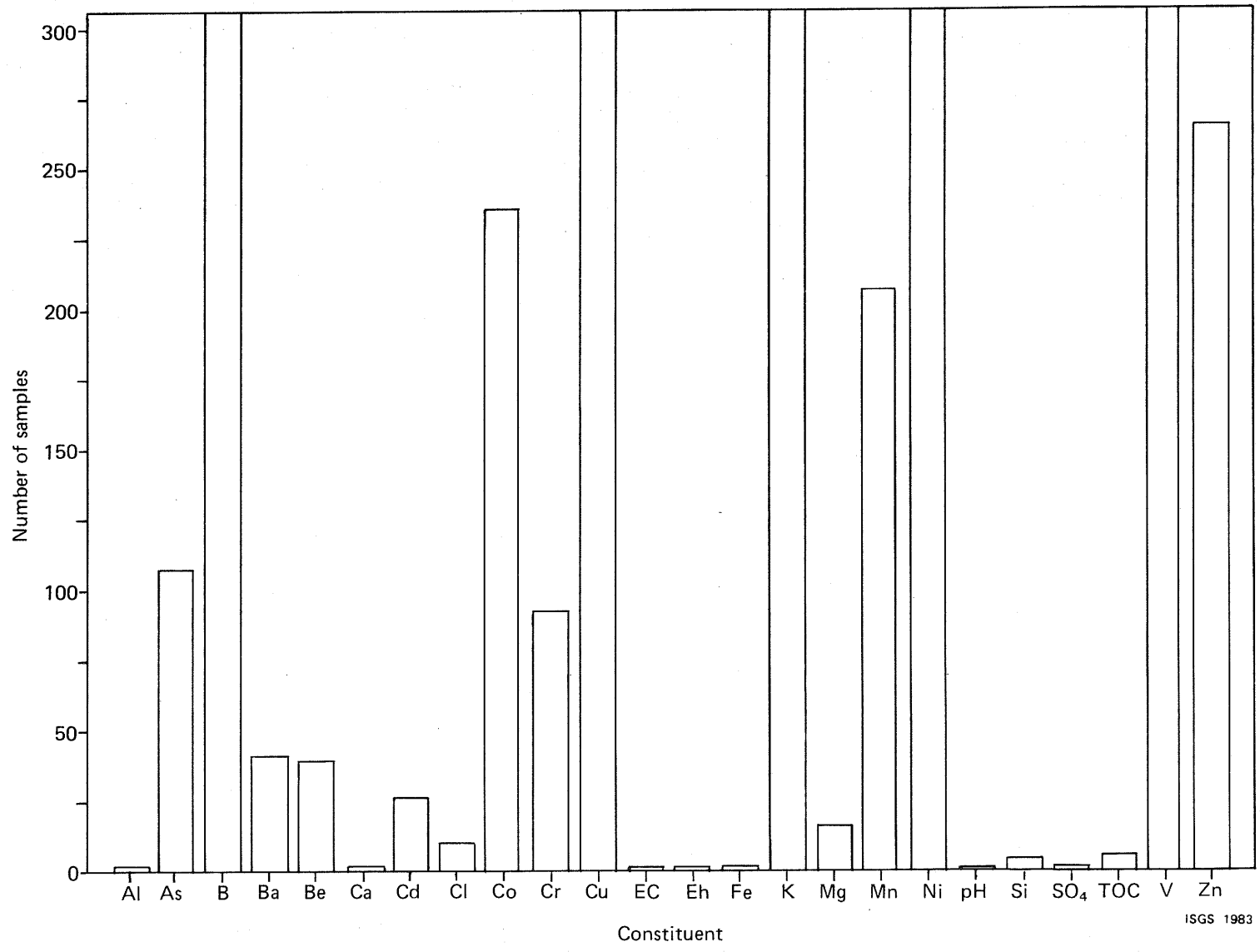


Figure 8. Number of samples at 10% error level and constituents for Little Dog extracts.



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Figure 9. Number of samples at 10% error level and constituents for Superior Washer extracts.

The variance of the population mean (\bar{y}) is:

$$V_{\bar{y}} = \frac{V_H}{H} + \frac{V_D}{D} + \frac{V_E}{H \cdot D} \quad (7)$$

where $V_{\bar{y}}$ = variance of the population mean for a particular extract constituent
H = number of sampling holes
D = number of depth zones
H•D = total number of samples.

By reviewing the costs of this study to collect, prepare, and analyze the samples for 30 constituents with the ASTM extraction method, a cost function was derived:

$$C = H(15 + 22.5L + 30D) \quad (8)$$

where C = cost to collect and analyze samples for all constituents
H = the number of holes
15 = the average cost/hole in dollars of drilling a hole
22.5 = the average cost of collecting split-spoon samples with depth
L = the average depth of the gob pile
30 = the average cost of preparing and analyzing a sample
D = the number of depth zones.

The variances in table 20 were used to estimate V_H , V_D , and V_E for extract constituent concentrations and to select different numbers and combinations of sample holes (H) and depths (D); the variance ($V_{\bar{y}}$) of the population as well as the cost involved in sampling the particular number of holes and depths were then estimated. This method of determining sample sizes is demonstrated in Case I (p. 52). Because there are differences between depth zones (GLM results in table 13), the entire hole must be sampled, even if only one composite sample per hole is collected. Accordingly, the L term in the cost function adjusts the cost of drilling a hole for gob piles of various depths.

Given the cost and variance functions (equations 7 and 8), the best combination of holes and depth zones to minimize the variance ($V_{\bar{y}}$) for a fixed cost can be determined, as demonstrated in Case II (p. 55). The mathematical procedure used to minimize equations 7 and 8 is shown in appendix B.

The final approach for determining sample sizes is shown in Case III (p. 56) where the variance ($V_{\bar{y}}$) is fixed and the best combinations of holes and depth zones are determined to minimize cost.

Determining sample size by minimizing costs or variances allows the variances determined in this study to be used as a guide for determining sample sizes for other gob piles, without the stipulation that the sampling scheme be identical to that used in this study. However, the two gob piles studied had different variances and means for extract constituents, and the data presented represent only estimates of sample sizes. This approach and the variances listed can be used as a sampling guide if preliminary data as to

Table 20. Variances for ASTM-A constituent concentrations.

Constituent	Little Dog			Constituent	Superior Washer		
	V_E^a	V_H^b	V_D^c		V_E	V_H	V_D
LA1	.08026	.06266	.03428	Al	6,221.00000	3,025.00000	-542.66667
LAs	.22328	.02187	.03074	As	.18992	.01559	.00782
LB	.65658	.32897	.15006	LB	.67249	.14623	.33222
Ba	.00040	-.00001	-.00003	Ba	.00062	.00012	.00016
Be	.00014	.00010	.00001	Be	.00005	.00002	.00001
Ca	3,842.00000	71,130.00000	1,101.57273	Ca	3,401.00000	52.20000	118.52222
LCd	.10315	.04678	-.00194	LCd	.14241	-.00236	.00856
LC1	.06629	.04229	.06616	LC1	.03359	.00150	.01454
LCo	.31363	.06949	.12195	LCo	.53565	.54800	.08371
LCr	.20515	.12830	.02603	LCr	.12919	.02918	.02427
LCu	.66680	.08712	.05982	LCu	.39588	.07387	.19056
LEC	.00944	.00516	.00809	EC	2,836,909.00000	509,045.37500	971,978.77778
Eh	1,264.60000	652.92167	194.88182	Eh	682.37000	-8.45875	18.63667
LFe	.17600	.05134	.04913	LFe	.13045	.00649	.02063
LK	.23560	.02246	-.00738	LK	.14500	.05078	.06248
Mg	618.21000	291.24667	309.03364	LMg	.02864	.04219	.00901
LMn	.05279	.00939	.00250	LMn	.13716	.02554	.00383
LNa	.31277	.13156	.51293	LNi	.11808	.08148	.03373
LNi	.07203	.03495	.05821	pH	.05493	.00125	.01619
pH	.20610	.04350	.07245	LSi	.01059	.00388	.00950
LSi	.01860	.00508	.00151	LSO ₄	.01702	.00316	.00297
LSO ₄	.01494	.01289	.00959	LTOC	.02118	.00826	.00822
LTOC	.03303	.02140	.01148	V	.15185	.00711	.02192
LV	.14235	.05769	.03750	LZn	.14657	.06387	.06754
LZn	.13356	.08936	.04960				

The L before constituent symbol indicates log transform data were used to calculate sizes.

^a sampling error variance

^b variance between holes

^c variance between depth zones

the variability of the gob pile are unavailable. These approaches could also be used if a two-tiered sampling plan were being used, with the results from this study acting as a guide to the first tier of the sampling scheme. Though the data set of this study is large for a first tier of a two-tiered sampling plan, this sort of approach is necessary for designing a sampling plan where more sophisticated questions (such as trends in concentrations due to depth or location) are to be answered.

CASE I

Selection of different numbers and combinations of sample holes and depth zones to minimize variance and cost

An example of a computer simulation using the program in appendix C was performed for Fe extract log concentrations and pH values from Little Dog and Superior Washer split-spoon samples. The results of this simulation are given in table 21. The following information was used to generate the results listed in the table:

- 1) Equations 7 and 8 were used to calculate the population variance and costs.
- 2) V_H , V_D , and V_E were obtained from table 20.
- 3) L in equation 8 was fixed, equal to 29 or 11, the average depth of the Little Dog and Superior Washer gob pile, respectively.
- 4) H and D in table 21 = 1, 3, 5, 7, or 9, where H = number of holes and D = number of depth zones.
- 5) n = total number of samples, (H•D).
- 6) Combinations of H and D were used to calculate various costs and variances.
- 7) Actual cost = cost for collection and analysis of the particular number of holes and samples.
- 8) $V_{\bar{y}}$ = estimated population variance.
- 9) Percent mean = $\frac{V_{\bar{y}}}{\bar{x}} \times 100$
where \bar{x} is the mean Fe log concentration or pH values of the 117 Little Dog and 63 Superior Washer extracts generated in this study.
- 10) Percent ± 2 standard errors ($S_{\bar{x}}$) = $\frac{(2)(\sqrt{V_{\bar{y}}})}{\bar{x}} \times 100$.

To further explain the simulation, an example of the calculations and explanation of the results using Fe as the constituent of interest and data from the Little Dog site are presented below. The program in appendix C allows iterations of various number combinations of holes and sampling depths. These numbers (1, 3, 5, 7, 9) could be changed to fulfill other investigators' sampling plans. For the sake of simplicity in this example, results (table 21) using the combination of 5 equally spaced holes and 3 equally spaced samples per hole will be illustrated.

Table 21. Number of samples to minimize variance and cost for Fe and pH in the Little Dog and Superior Washer ASTM-A extracts.

		Little Dog				
D ^a	H ^b	n	Actual cost	$V_{\bar{y}}^c$	Percent mean	Percent $\pm 2S_{\bar{x}}$
LFe		$V_E = .17600$	$V_H = .05134$	$V_D = .04913$	$\bar{x} = 2.58265$	
1	1	1	\$ 697.50	.27647	10.70490	40.71819
3	1	3	\$ 757.50	.12638	4.89355	27.53020
5	1	5	\$ 817.50	.09637	3.73128	24.03955
7	1	7	\$ 877.50	.08350	3.23317	22.37749
9	1	9	\$ 937.50	.07635	2.95644	21.39841
1	3	3	\$2,092.50	.12491	4.83651	27.36926
3	3	9	\$2,272.50	.05305	2.05392	17.83565
5	3	15	\$2,452.50	.03867	1.49740	15.22883
7	3	21	\$2,632.50	.03251	1.25890	13.96343
9	3	27	\$2,812.50	.02909	1.12639	13.20815
1	5	5	\$3,487.50	.09460	3.66283	23.81801
3	5	15	\$3,787.50	.03838	1.48599	15.17070
5	5	25	\$4,087.50	.02713	1.05063	12.75620
7	5	35	\$4,387.50	.02237	.86404	11.56816
9	5	45	\$4,687.50	.01964	.76038	10.85208
pH		$V_E = .20610$	$V_H = .04350$	$V_D = .07245$	$\bar{x} = 2.60670$	
1	1	1	\$ 697.50	.32205	12.35470	43.54122
3	1	3	\$ 757.50	.13635	5.23075	28.33130
5	1	5	\$ 817.50	.09921	3.80596	24.16666
7	1	7	\$ 877.50	.08329	3.19534	22.14332
9	1	9	\$ 937.50	.07445	2.85610	20.93492
1	3	3	\$2,092.50	.15565	5.97115	30.27008
3	3	9	\$2,272.50	.06155	2.36122	19.03500
5	3	15	\$2,452.50	.04273	1.63924	15.86008
7	3	21	\$2,632.50	.03466	1.32981	14.28499
9	3	27	\$2,812.50	.03018	1.15791	13.32977
1	5	5	\$3,487.50	.12237	4.69444	26.83962
3	5	15	\$3,787.50	.04659	1.78732	16.56095
5	5	25	\$4,087.50	.03143	1.20589	13.60313
7	5	35	\$4,387.50	.02494	.95671	12.11643
9	5	45	\$4,687.50	.02133	.81828	11.20558

^a sampling depth

^b sampling location

^c population variance

Table 21. continued.

Superior Washer						
D	H	n	Actual cost	$V_{\bar{y}}$	Percent mean	Percent $\pm 2S_{\bar{x}}$
LFe		$V_E = .13045$	$V_H = .00649$	$V_D = .02063$	$\bar{x} = 2.81320$	
1	1	1	\$ 292.50	.15757	5.60109	28.22059
3	1	3	\$ 352.50	.05685	2.02083	16.95097
5	1	5	\$ 412.50	.03671	1.30478	13.62065
7	1	7	\$ 472.50	.02807	.99790	11.91167
9	1	9	\$ 532.50	.02328	.82741	10.84650
1	3	3	\$ 877.50	.06628	2.35592	18.30247
3	3	9	\$1,057.50	.02353	.83657	10.90640
5	3	15	\$1,237.50	.01499	.53270	8.70307
7	3	21	\$1,417.50	.01132	.40247	7.56481
9	3	27	\$1,597.50	.00929	.33012	6.85122
1	5	5	\$1,462.50	.04802	1.70688	15.57871
3	5	15	\$1,762.50	.01687	.59972	9.23430
5	5	25	\$2,062.50	.01064	.37829	7.33400
7	5	35	\$2,362.50	.00797	.28339	6.34776
9	5	45	\$2,662.50	.00649	.23067	5.72693
pH		$V_E = .05493$	$V_H = .00125$	$V_D = .01619$	$\bar{x} = 2.12920$	
1	1	1	\$ 292.50	.07237	3.39893	25.26928
3	1	3	\$ 352.50	.02496	1.17211	14.83907
5	1	5	\$ 412.50	.01547	.72675	11.68463
7	1	7	\$ 472.50	.01141	.53588	10.03359
9	1	9	\$ 532.50	.00915	.42984	8.98622
1	3	3	\$ 877.50	.03492	1.63990	17.55213
3	3	9	\$1,057.50	.01192	.55968	10.25394
5	3	15	\$1,237.50	.00732	.34363	8.03471
7	3	21	\$1,417.50	.00535	.25104	6.86747
9	3	27	\$1,597.50	.00425	.19961	6.12362
1	5	5	\$1,462.50	.02743	1.28809	15.55589
3	5	15	\$1,762.50	.00931	.43719	9.06269
5	5	25	\$2,062.50	.00569	.26701	7.08250
7	5	35	\$2,362.50	.00413	.19408	6.03822
9	5	45	\$2,662.50	.00327	.15356	5.37103

The estimated population variance was determined from equation 7 and the variances listed in table 20:

$$\begin{aligned}
 V_{\bar{y}} &= \frac{V_H}{H} + \frac{V_D}{D} + \frac{V_E}{H \cdot D} \\
 &= \frac{.05134}{5} + \frac{.04913}{3} + \frac{.17600}{15} \\
 &= .03838
 \end{aligned}$$

Because the population variance is the square of the standard error of the population mean, the results generated by the simulation can be treated similarly to those of the t distribution method of estimating sample sizes. The logic behind the t distribution method dictates that the proportion (in percent) that the sample mean approximates the population mean within two standard errors ($t_{\alpha/2, (n-1)} = 2$) at a 95% confidence level can be estimated for the various sample sizes generated by the simulation. The results are listed in table 21 under the column heading percent $\pm 2S_{\bar{x}}$. For this example (5 holes, 3 depths) the percent $\pm 2S_{\bar{x}}$ was equal to:

$$\frac{(2) \sqrt{(.03838)}}{2.58265} \times 100 = 15.17\%$$

The result of this calculation indicates that the population mean, with a 95% certainty, will be within $\pm 15.17\%$ of the sample mean generated by these 15 samples.

Another possible way of determining the precision of the sample is by calculating the ratio of the sample mean variance to the sample mean (percent mean) (table 21). For this example, the percent mean = $\frac{.03838}{2.58265} \times 100 = 1.48\%$ -- the variance of the sample mean is 1.48% of the sample mean. This is similar to the coefficient of variation that could also be used.

The cost of preparing and analyzing the 15 samples was calculated using equation 8 where:

$$\begin{aligned}
 C &= H(15 + 22.5L + 30D) \\
 &= 5 [15 + (22.5)(29) + (30)(3)] \\
 &= \$3787.50 \text{ (i.e., the cost of preparing and analyzing the 15 samples).}
 \end{aligned}$$

The other simulations determine the variances, cost, and precision requirements similarly.

CASE II

Fixing cost to determine the number of holes and depth zones to minimize variance

The Case II simulation used a cost function fixed at \$1,000, \$5,000, \$10,000, \$15,000, and \$25,000 for collection of split-spoon samples, sample preparation, and analysis of the ASTM extracts to determine the concentrations of 30 constituents. Equations 2, 3, and 11 in appendix B and the computer

program in appendix D were used in this simulation. An example of the simulation for Fe log concentrations and pH values from the ASTM-A extract procedure for the Little Dog and Superior Washer sites is shown in table 22. The following define or explain the results in the table:

- 1) Cost is fixed at either \$1,000, \$5,000, \$10,000, \$15,000, or \$25,000.
- 2) D and H = the calculated depth zones and holes, as derived from equations 2, 3, and 11, respectively, in appendix B.
- 3) n = total number of samples, (H•D).
- 4) Actual cost, $V_{\bar{y}}$, percent mean, percent $\pm 2S_{\bar{x}}$ are derived similarly to Case I.
- 5) L is fixed in equation 2 as 29 and 11 for the Little Dog and Superior Washer sites, respectively, and represents the average depths of the two gob piles.

Several observations can be made from this simulation:

- 1) Different costs result in different sample sizes; thus, the estimate of the population variance will vary.
- 2) Depending on the variance associated with the analyte being considered, for a given cost, differences in the number of holes and depth zones as well as the accuracy in estimating the population variance will change due to differences between constituent and gob pile variability.

CASE III

Fixing variance to determine the number of holes and depth zones to minimize cost

In this simulation the variance ($V_{\bar{y}}$) function was fixed at 10%, 5%, and 1% of the sample mean for each extract constituent and the number of holes and depth zones to minimize cost were determined. An example of the simulation for Fe log concentrations and pH values generated from the ASTM-A extract procedure for the Little Dog and Superior Washer sites is shown in table 23. The definitions of the symbols used in this table are the same as those explained in the two previous cases. Equations 1, 6, and 16 in appendix B and the computer program in appendix E were used in this simulation.

The results of this simulation are as expected. As the variance is decreased to insure accuracy, the sample sizes and the costs increase accordingly. As was observed in the other simulations, differences between extract constituents and gob piles are apparent. When determining a sampling plan where several constituents will be investigated, a compromise between cost and accuracy would have to be made, depending on the specific chemical constituents of interest.

In summary, these simulations are guides to developing a sampling plan for collection of samples from gob piles for use in leaching studies. One must remember that differences exist for each extract constituent, and thus costs and the number of samples required to estimate the population variance for a particular constituent will vary. Compromises would have to be made if

Table 22. Number of samples to minimize variance at a fixed cost for Fe and pH in the Little Dog and Superior Washer ASTM-A extracts.

Cost	D	H	n	Actual cost	$V_{\bar{y}}$	Percent mean	Percent $\pm 2S_{\bar{x}}$
<u>Little Dog</u>							
LFe	$V_E = .17600$		$V_H = .05134$		$V_D = .04913$	$\bar{x} = 2.58265$	
\$ 1,000.00	10	1	10	\$ 967.50	.07385	2.85958	21.04498
\$ 5,000.00	15	4	60	\$ 4,470.00	.01904	.73737	10.68660
\$10,000.00	20	8	160	\$10,140.00	.00997	.38619	7.73391
\$15,000.00	24	11	264	\$15,262.50	.00738	.28579	6.65308
\$25,000.00	30	16	480	\$25,080.00	.00521	.20185	5.59129
<u>Superior Washer</u>							
pH	$V_E = .20610$		$V_H = .04350$		$V_D = .07245$	$\bar{x} = 2.60670$	
\$ 1,000.00	13	1	13	\$ 1,057.50	.06493	2.49077	19.55021
\$ 5,000.00	20	4	80	\$ 5,070.00	.01707	.65499	10.02544
\$10,000.00	26	7	182	\$10,132.50	.01013	.38874	7.72348
\$15,000.00	31	9	279	\$14,377.50	.00791	.30342	6.82344
\$25,000.00	39	14	546	\$25,725.00	.00534	.20495	5.60794
<u>Superior Washer</u>							
LFe	$V_E = .13045$		$V_H = .00649$		$V_D = .02063$	$\bar{x} = 2.81320$	
\$ 1,000.00	17	1	17	\$ 772.50	.01538	.54660	8.81589
\$ 5,000.00	27	5	135	\$ 5,362.50	.00303	.10765	3.91232
\$10,000.00	35	8	280	\$10,500.00	.00187	.06635	3.07151
\$15,000.00	42	10	420	\$15,225.00	.00145	.05157	2.70789
\$25,000.00	53	13	689	\$24,082.50	.00108	.03831	2.33400
<u>Superior Washer</u>							
pH	$V_E = .05493$		$V_H = .00125$		$V_D = .01619$	$\bar{x} = 2.12920$	
\$ 1,000.00	29	1	29	\$ 1,132.50	.00370	.17389	5.71552
\$ 5,000.00	50	3	150	\$ 5,287.50	.00111	.05198	3.12480
\$10,000.00	69	4	276	\$ 9,330.00	.00075	.03504	2.56584
\$15,000.00	83	5	415	\$13,762.50	.00058	.02712	2.25715
\$25,000.00	106	7	742	\$24,097.50	.00041	.01904	1.89113

Table 23. Number of samples to minimize cost at a fixed variance for Fe and pH in the Little Dog and Superior Washer ASTM-A extracts.

Proportion of mean	D	H	n	Actual cost	$V_{\bar{y}}$	Percent mean	Percent $\pm 2S_{\bar{x}}$
<u>Little Dog</u>							
	LFe	$V_E = .17600$	$V_H = .05134$	$V_D = .04913$	$\bar{x} = 2.58265$		
.100	12	2	24	\$ 2,055.00	.03710	1.43641	14.91546
.050	15	4	60	\$ 4,470.00	.01904	.73737	10.68660
.010	36	22	792	\$38,445.00	.00392	.15180	4.84886
	pH	$V_E = .20610$	$V_H = .04350$	$V_D = .07245$	$\bar{x} = 2.60670$		
.100	15	2	30	\$ 2,235.00	.03345	1.28323	14.03256
.050	19	4	76	\$ 4,950.00	.01740	.66751	10.12077
.010	50	20	1,000	\$43,350.00	.00383	.14693	4.74836
<u>Superior Washer</u>							
	LFe	$V_E = .13045$	$V_H = .00649$	$V_D = .02063$	$\bar{x} = 2.81320$		
.100	22	1	22	\$ 1,327.50	.01336	.47481	8.21653
.050	23	1	23	\$ 1,357.50	.01306	.46419	8.12418
.010	33	4	132	\$ 6,630.00	.00324	.11503	4.04415
	pH	$V_E = .05493$	$V_H = .00125$	$V_D = .01619$	$\bar{x} = 2.12920$		
.100	32	1	32	\$ 1,627.50	.00347	.16309	5.53522
.050	33	1	33	\$ 1,657.50	.00341	.15993	5.48128
.010	38	1	38	\$ 1,807.50	.00312	.14661	5.24808

several constituents are investigated. If "x" dollars were available for the investigation, an average of the number of holes and depth classes for all constituents that provide a minimum variance (V_y) would be used in the sample collection process. Conversely, if the variances for particular constituents must be kept to a minimum, the average cost to collect and analyze the samples for the constituents could be used to estimate the cost of the sampling plan.

The results of the computer simulation can act as a guide for future sampling plans. However, the cost function was derived for this particular study and would have to be changed to reflect the costs accrued by other investigators. This cost function is also for the collection of split spoons where an entire hole is sampled. By using other sampling techniques, such as auger cuttings, the costs may decrease.

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APPENDIX A**Extract constituents and their detection limits (mg/L)**

Constituent	Detection Limit
Al	.05
As	.05
B	.002
Ba	.001
Be	.002
Ca	.01
Cd	.01
Cl	1.0
Co	.01
Cr	.03
Cu	.01
Fe	.03
K	1.03
Mg	.003
Mn	.01
Mo	.01
Na	1.42
Ni	.01
Pb	.03
Sb	.03
Se	.05
Si	.03
Sn	.11
SO ₄	2.0
TOC [#]	2.0
V	.04
Zn	.01

APPENDIX B
Formulas and their derivation

Define the cost function as: $C = 15H + 30HD + 22.5LH$ (1)
 $= H(15 + 22.5L + 30D)$

Define the population variance for a particular extract constituent as:

$$V_{\bar{y}} = \frac{V_H}{H} + \frac{V_D}{D} + \frac{V_E}{S} \quad (2)$$

where D = the number of depth classes (on average)

H = the number of holes

S = the number of samples taken = $H \cdot D$

L = the average depth of the site

V_H = the estimated variance among holes

V_D = the estimated variance among depth classes

V_E = the estimated sampling error variance.

Note the following relationships:

from equation (1) for a fixed C :

$$H = C / (15 + 22.5L + 30D) \quad (3)$$

$$D = \left(\frac{C}{H} - 15 - 22.5L \right) / 30 \quad (4)$$

from equation (2) for a fixed $V_{\bar{y}}$:

$$H = \frac{DV_H + V_E}{DV_{\bar{y}} - V_D} \quad (5)$$

$$D = \frac{HV_D + V_E}{HV_{\bar{y}} - V_H} \quad (6)$$

Minimize $V_{\bar{y}}$ for a fixed cost C . This minimization requires the use of the Lagrange multiplier (λ) method where the cost function is the constant.

Let $f(H,D)$ be the function to be minimized:

$$f(H,D) = \frac{V_H}{H} + \frac{V_D}{D} + \frac{V_E}{HD} - \lambda \{ H(15 + 30D + 22.5L) - C \} \quad (7)$$

The partial derivatives are:

$$\frac{\partial f}{\partial H} = \frac{-V_H}{H^2} - \frac{V_E}{H^2 D} - \lambda(15 + 22.5L + 30D) \quad (8)$$

$$\frac{\partial f}{\partial D} = \frac{-V_D}{D^2} - \frac{V_E}{HD^2} - 30H\lambda \quad (9)$$

$$\frac{\partial f}{\partial \lambda} = -H(15 + 30D + 22.5L) + C \quad (10)$$

Set each of these to zero (resulting in three equations with three unknowns) and solve for D:

$$D = \sqrt{\frac{(15 + 22.5L)V_E + CV_D}{30V_H}} \quad (11)$$

and solve for H by substituting for D in equation (3).

Minimize the cost C for a fixed $V_{\bar{y}}$:

$$\text{Let } g(H,D) = H(15 + 22.5L + 30D) - \lambda\left(\frac{V_H}{H} + \frac{V_D}{D} + \frac{V_E}{HD} - V_{\bar{y}}\right) \quad (12)$$

The partial derivatives are:

$$\frac{\partial g}{\partial H} = 15 + 22.5L + 30D + \frac{\lambda V_H}{H^2} + \frac{\lambda V_E}{H^2 D} \quad (13)$$

$$\frac{\partial g}{\partial D} = 30H + \frac{\lambda V_D}{D^2} + \frac{\lambda V_E}{HD^2} \quad (14)$$

$$\frac{\partial g}{\partial \lambda} = \frac{-V_H}{H} - \frac{V_D}{D} - \frac{V_E}{HD} + V_{\bar{y}} \quad (15)$$

Set each derivative to zero and solve for H:

$$\text{Let } E = .5 + .75L$$

$$a = EV_{\bar{y}}^2 + V_D V_{\bar{y}}$$

$$b = -2V_D V_H - 2EV_H V_{\bar{y}}$$

$$c = EV_H^2 - V_E V_H \quad H = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (16)$$

and solve for D by substituting for H in equation (6).

APPENDIX C

Computer program to calculate cost and variance for combinations of holes and depth classes

```
PROGRAM COSTVO(INCOST,OUT,INPUT,OUTPUT,TAPE7=INCOST,TAPE8=OUT)

* COMPILATION:  FTN5 ON CDC CYBER 175 UNDER NOS 1.4

* PURPOSE:  CALCULATE COST AND VARIANCE FOR VARIOUS COMBINATIONS OF
*          HOLE (HI) AND DEPTH CLASSES (DI)

* INPUT FILE:  INCOST -- VARIANCE (VH, VD, VE) FILE WITH MEANS FOR EACH
*          CONSTITUENT AT EACH SITE

CHARACTER TITLE(2)*10,LABEL*4
INTEGER NK(2),DI,HI,I,J,S
REAL C,VH,VE,VD,LL(2),E,D,H,C2,VY,X,K,XP,L
DATA TITLE/'SITE=LD','SITE=SW'/,NK/25,24/
DATA LL/29.,11./
DO 500 I=1,2
  L=LL(I)
  WRITE (8,1000)TITLE(I),L
  DO 490 J=1,NK(I)
    READ(7,*,END=600)LABEL,VE,VH,VD,X
    WRITE(8,1100)LABEL,VE,VH,VD,X
    IF(X.LE.0)X=ABS(X)
    IF(VH.LE.0)VH=0.
    IF(VD.LE.0)VD=0
    DO 450 HI=1,9,2
      DO 450 DI=1,9,2
        S=DI*HI
        C=HI*(15.+22.5*L +30*DI)
        VY=VE/FLOAT(S) + VD/FLOAT(DI) + VH/FLOAT(HI)
        XP=100.*VY/X
        XP2=200.*SQRT(VY)/X
        WRITE(8,1250)HI,DI,S,C,VY,XP,XP2
450      CONTINUE
490    CONTINUE
500  CONTINUE

PRINT*,'OUTPUT IN FILE OUT'
600  CONTINUE
STOP
1000 FORMAT(1H1,' FOR ',A10,' AVG DEPTH= ',F5.1,
+ ' VARIOUS HOLE AND DEPTH COMBINATIONS',/
+ 10X,'ELEMENT',11X,'VE',11X,'VH',11X,'VD',11X,'MEAN')

1100  FORMAT(//7X,A10,4F15.5,//,28X
+ 'HI',9X,'DI',7X,'S',9X,'ACOST',9X,'VARY',9X,
+ 'PCNT MEAN',8X,'PCNT +/-2STDERR',/)

1250  FORMAT(20X,3I10,5X,'$',F8.2,F15.5,2F15.5)
END
```

APPENDIX D

Computer program to calculate sample sizes for fixed cost

PROGRAM COSTF(INCOST,OUT,INPUT,OUTPUT,TAPE7=INCOST,TAPE8=OUT)

- * COMPILATION: FTN5 ON CDC CYBER 175 UNDER NOS 1.4
- * PURPOSE: CALCULATE BEST HOLE (H) AND DEPTH CLASSES (D) FOR FIXED COST (C)
- * INPUT FILE: INCOST -- VARIANCE (VH, VD, VE) FILE WITH MEANS FOR EACH
- * CONSTITUENT AT EACH SITE

```

CHARACTER TITLE(2)*10,LABEL*4
INTEGER NK(2),DI,HI,I,J,S
REAL CO(5),C,VH,VE,VD,LL(2),E,D,H,C2,VY,X,K,XP,L
DATA TITLE/'SITE=LD','SITE=SW'/,NK/25,24/
DATA LL/29.,11./,CO/1000,5000,10000,15000,25000/
DO 500 I=1,2
  L=LL(I)
  WRITE(8,1000)TITLE(I),L
  DO 490 J=1,NK(I)
    READ(7,*,END=600)LABEL,VE,VH,VD,X
    WRITE(8,1100)LABEL,VE,VH,VD,X
    IF(X.LE.0)X=ABS(X)
    IF(VH.LE.0)GO TO 490
    IF(VD.LE.0)VD=0
    DO 450 KK=1,5
      C=CO(KK)
      E=(15. + 22.5*L)*VE + C*VD
      E=E/(30*VH)
      D=SQRT(E)
      H=C/(15.+30*D+22.5*L)
      DI=D+.500000001
      HI=H+.500000001
      S=DI*HI
      C2=HI*(15. + 22.5 *L + 30.*DI)
      VY=VE/FLOAT(S) + VD/FLOAT(DI) + VH/FLOAT(HI)
      XP2=200.*SQRT(VY)/X
      XP=100.*VY/X
      WRITE(8,1200)C,D,H,DI,HI,S,C2,VY,XP,XP2
450     CONTINUE
490     CONTINUE
500     CONTINUE
        PRINT*,'OUTPUT IN FILE OUT'
600     CONTINUE
        STOP

1000    FORMAT(1H1,' FOR ',A10,' AVG DEPTH= ',F5.1,
+ ' BEST HOLE,DEPTH# COMBOS FOR 5 FIXED COSTS',/
+ 10X,'ELEMENT',11X,'VE',11X,'VH',11X,'VD',11X,'MEAN')

1100    FORMAT(//7X,A10,4F15.5,//,10X,'COST',8X,'D',8X,'H',8X,
+ 'DI',9X,'HI',7X,'S',9X,'ACOST',9X,'VARY',9X,
+ 'PCNT MEAN',8X,'PCNT +/-2STDERR',/)

1200    FORMAT(5X,'$',F8.2,2F10.2,3I10,4X,'$',F8.2,3F15.5)
        END

```

APPENDIX E

Computer program to calculate sample sizes for fixed variance

```

PROGRAM COSTV(INCOST,OUT,INPUT,OUTPUT,TAPE7=INCOST,TAPE8=OUT)

* COMPILATION:  FTN5 ON CDC CYBER 175 UNDER NOS 1.4

* PURPOSE:  CALCULATE BEST HOLE (H) AND DEPTH CLASSES (D) FOR FIXED VARIANCE
            VY = PCT * SAMPLE MEAN (X)

* INPUT FILE:  INCOST -- VARIANCE (VH, VD, VE) FILE WITH MEANS FOR EACH
*              CONSTITUENT AT EACH SITE

CHARACTER  TITLE(2)*10,LABEL*4
INTEGER  NK(2),DI,HI,I,J,S
REAL  PCT(4),C,VH,VE,VD,LL(2),E,D,H,C2,VY,X,K,XP,L
DATA  TITLE/'SITE=LD','SITE=SW'/,NK/25,24/
DATA  LL/29.,11./,PCT/.10,.05,.10,.001/
DO 500 I=1,2
  L=LL(I)
  WRITE(8,1000)TITLE(I),L
  DO 490 J=1,NK(I)
    READ(7,*,END=600)LABEL,VE,VH,VD,X
    WRITE(8,1100)LABEL,VE,VH,VD,X
    IF(X.LE.0)X=ABS(X)
    IF(VH.LE.0)GO TO 490
    IF(VD.LE.0)GO TO 490
    DO 450 KK=1,4
      K=PCT(KK)/X
      E=.5 + .75*L
      A=E*K*K*+VD*K
      B=-2.*VH*(VD+E*K)
      CC=E*VH*VH-VE*VH
      DD=B**2.-4*A*CC
      IF(DD.LE.0)GO TO 450
      H=(-B+SQRT(DD))/(2.*A)
      HI=H+.500001
      IF(HI.LE.0)HI=1
      D=(H*VD + VE)/(H*K - VH)
      DI=D+.500001
      IF(DI.LE.0)DI=1
      C=HI*(15. + 22.5 * L +30.*DI)
      S=DI*HI
      VY=VE/FLOAT(S) + VD/FLOAT(DI) + VH/FLOAT(HI)
      XP=100.*VY/X
      XP2=200.*SQRT(VY)/X
      WRITE(8,1250)PCT(KK),H,HI,D,DI,S,C,VY,XP,XP2
450      CONTINUE
490      CONTINUE
500      CONTINUE
        PRINT*, 'OUTPUT IN FILE OUT'
600      CONTINUE
        STOP

```



```
1000  FORMAT(1H1,' FOR ',A10,' AVG DEPTH= ',F5.1,  
+ ' BEST HOLE,DEPTH# COMBOS FOR 3 FIXED VARIANCES',/  
+ 10X,'ELEMENT',11X,'VE',11X,'VH',11X,'VD',11X,'MEAN')  
  
1100  FORMAT(//7X,A10,4F15.5,//,' PRP MEAN',5X,'H',9X,'HI',9X,'D',9X  
+,'DI',9X,'S',9X,'ACTCOST',9X,'VAR Y',9X,'PCT MEAN',4X,  
+ 'PCT +-2STDERR',/)  
  
1250  FORMAT(2X,F5.3,F10.2,I10,F10.2,2I10,5X,'$',F10.2,3F15.5)  
      END
```